Investigation of the electrocatalytic oxidation of ethanol under high temperature polymer electrolyte fuel cell conditions

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Présentée par Christiane NIETHER

Étude de l'oxydation électrocatalytique de l'éthanol dans les conditions d'une pile à combustible à membrane électrolyte polymère haute température

Soutenue le 17 Décembre 2015 devant le jury composé de

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Etude de l'oxydation électrocatalytique de l'éthanol dans les conditions d'une pile à combustible à membrane électrolyte polymère haute température

L'oxydation électrochimique de l'éthanol (EOR) est une réaction d'intérêt pour la recherche fondamentale d'une part, et pour son utilisation potentielle dans les piles à combustible à alcool direct d'autre part. Le mécanisme de la réaction n'a pas encore été complètement résolu. La distribution des quatre produits d'oxydation - acétdownyléhyde, acide acétique, acétate d'éthyle et dioxyde de carbone (CO₂) - est fortement influencée par les conditions de réaction. La scission de la liaison C-C en particulier est d'une importance clé pour l'oxydation complète en CO₂, ce qui permet une utilisation effective dans les piles à combustible. La cinétique de cette étape de réaction peut être améliorée par la température élevée. Par conséquent l'utilisation de la technologie de pile à combustible à membrane échangeuse de protons à des températures entre 120 et 200 °C (HT-PEMFC) permet d'optimiser la réaction. Jusqu'à présent, des études sur la EOR ont été menées en installations expérimentales demi-cellule à des températures allant jusqu'à 100 °C dans un électrolyte aqueux liquide, ou avec un électrolyte gazeux à des températures supérieures à 100 °C dans des cellules HT-PEMFC ou des piles simples.

L'objet de cette étude était le développement d'une installation expérimentale demi-cellule pour mesurer l'EOR en phase gazeuse à des températures comprises entre 120 et 180 °C. Le travail effectué pour cette thèse faisait partie d'un projet ayant pour objectif une utilisation efficace du bio-éthanol dans les piles à combustible (EUBECELL), une collaboration des Instituts Carnot Energies du Futur et de Chimie et Environnement et Développement Durable, de l'Institut Fraunhofer de Technologie Chimique (ICT), et les partenaires industriels Südzucker et Fumatech. Ce travail a été co-supervisé par Fraunhofer ICT et l'Université de Montpellier. Le projet faisait partie du Programme Inter-Carnot-Fraunhofer (PICF) financé par l'Agence nationale française de recherche (ANR) et le Ministère fédéral allemand de l'Éducation et de la Recherche (BMBF). Son objectif est l'étude et l'optimisation des catalyseurs de DEFC et des conditions réactionnelles pour une application dans les piles à combustibles à température élevée et les piles à combustible alcalines.
Installation expérimentale de spectrométrie de masse électrochimique différentielle (DEMS)

Une cellule spéciale DEMS à trois électrodes a été créée afin d'étudier la réactivité des électrodes à petite échelle, dans des conditions proches de celles d'une HT-PEMFC et en particulier pour l'évaluation de l'EOR. Comme le système modèle doit être aussi proche que possible d'une réelle HT-PEMFC, l'électrode de travail (WE) est une électrode à diffusion de gaz (GDE), composée d'une couche de catalyseur sur une couche de diffusion de gaz (GDL). Avec une membrane polybenzimidazole (PBI) dopée avec de l'acide phosphorique [1–4], elle forme un ensemble membrane-électrode (MEA) du HT-PEMFC. Tenant compte des conditions de fonctionnement d'une HT-PEMFC classique, le dispositif expérimental développé permet de travailler sous pression atmosphérique jusqu'à 180 °C.

Un spectromètre de masse (MS), utilisé pour détecter les produits volatils de l'EOR, est relié à la cellule à trois électrodes par un capillaire chauffé placé à la sortie de gaz. De cette façon, les produits volatils formés sur la surface active de l'électrode de travail peuvent être pompés dans le MS, ce qui permet la détermination et quantification des composés produits par mesure de leurs courants de masse correspondants [5].

La conception de la cellule est détaillée dans la Figure 0.1. Elle se compose de trois parties principales superposées en polyéthéréthercétone (PEEK) [6]: une partie supérieure, un corps et un fond. Le fond de la cellule est la partie la plus complexe. Il reçoit l'électrode de travail et la membrane d'électrolyte polymère. C'est le lieu où arrivent les produits de départ et où sont formés les produits volatils. Il est constitué d'un cylindre plat contenant une chambre conique avec une buse en son centre (1) qui se termine au-dessous de l'électrode de travail (2) et à travers laquel les gaz réactifs entrent. Le combustible liquide est évaporé en utilisant un dispositif de chauffage microstructuré chauffé électriquement.

L'électrode de travail (WE) est supportée par un tamis en PEEK (3) qui est placé au-dessus de la chambre conique. Entre le support en PEEK et la WE une maille d'or (4) facilite la conduction d'électrons au contact extérieur de la cellule. La WE est placée sur le dessus de celui-ci avec la couche de catalyseur vers le haut, en face de la membrane PBI (5). Depuis le dessous de la chambre conique, la sortie de gaz (6) mène à l'extérieur et permet de rejoindre le MS.
Figure 0.1: La cellule HT-PEM DEMS: (1) buse, entrée de les gaz réactifs, (2) électrode de travail (WE), (3) tamis en PEEK, (4) maille d’or, (5) membrane PBI, (6) sortie de gaz et connexion au MS, (7) filtre en verre borosilicate, (8) contre-électrode (CE), (9) Luggin capillaire, (10) électrode de référence (RE), (11) plaque de chauffage en cuivre, (12) chauffage à l'intérieur de l'électrolyte, (13) et (14) thermocouples, (15) isolation thermique.
La membrane PBI dopée à l’acide phosphorique et le corps de cellule sont empilés sur le fond de la GDE. Les trois parties de l’installation expérimentale sont empilées au-dessus d’une plaque de chauffage en cuivre. Un joint plat en PTFE est utilisé pour sceller la connexion entre le fond de la cellule et le corps de la cellule. Le corps de la cellule contient de l’acide phosphorique (H\textsubscript{3}PO\textsubscript{4}) concentré. Sur la face inférieure, il présente une ouverture contenant un filtre en verre borosilicate amovible (7), qui permet le contact de la solution électrolytique avec la membrane, encombrant la membrane et la WE pour réduire la résistance ohmique et la résistance de contact. Une contre-électrode (CE) de Pt (8) et un capillaire (9) reliant à une électrode de référence (10) sont mis en suspension à l’intérieur du corps de la cellule.

La partie inférieure de la cellule est chauffée par le dessous par une plaque de chauffage en cuivre (11). Le corps de la cellule est chauffé par un chauffage à l’intérieur de l’électrolyte (12). La température à l’intérieur de la cellule est mesurée par deux thermocouples (13 et 14). En outre, la cellule électrochimique est complètement isolée thermiquement (15).

**Effet de la température sur le noir de platine**

Des mesures de référence ont été menées sous courant d’azote sur GDE revêtue du catalyseur Noir de platine dans la plage de température entre 120 °C et 180 °C. Elles montrent des signes de dégradation, en particulier à des températures de 160 °C et plus. Ces signes sont les suivants: 1) la formation de petites quantités de CO\textsubscript{2}, détectables par spectrométrie de masse, qui ne peut venir que de l’oxydation de la GDL comme aucun support de carbone pour le catalyseur est présent, 2) les changements dans la forme de la voltammetrie cyclique (CV) et 3) la perte des caractéristiques typiques du Pt, qui est réversible dans une certaine mesure et révèle un effet supplémentaire de l’électrolyte d’acide phosphorique concentré.

On a pu montrer que, dans des conditions de haute température et d’acide phosphorique concentré, le matériau de carbone de la GDL n’est pas totalement inerte. En conséquence, les mesures de l’oxydation de l’éthanol ont été réalisées seulement à des températures allant jusqu’à 160 °C. Les mesures en utilisant des catalyseurs supportés par du carbone ont été limitées à 150 °C.
C, un compromis entre cinétique améliorée à haute température et une dégradation admissible. On a pu montrer que la quantité de CO$_2$ formée par corrosion de carbone est négligeable comparé à celle formée par l'EOR.

La forme des courbes de CV mesurées à des températures dans la plage de 120 à 160 °C avec un mélange éthanol/eau de concentration 10,9 M (500 g/l) indique une relation approximativement linéaire entre le courant et le potentiel dans la gamme de potentiel observée (Figure 0.2). Habituellement, une diminution du courant d'oxydation de l'éthanol avec un potentiel croissant est observé après le début de la formation d'oxyde sur la surface de Pt$^{[7-12]}$.

Figure 0.2: Mesures CV (cycle 5) de l'oxydation de l'éthanol en phase gazeuse sur le catalyseur noir de Pt à des températures dans la plage de 120 à 160 °C, 10,9 M de l'éthanol 25 µl/min (l) vitesse de balayage 10 mV/s.

Les MSCVs montrent que des quantités significatives de produits secondaires acétaldéhyde et acétate d'éthyle sont produites à toutes les températures étudiées, ce qui est attendu d'après des mesures antérieures de l'EOR. L'efficacité de la formation de CO$_2$ déterminée à partir des CV et
MSCVs pour m/z = 22 est 10 % à 120 °C et 24 % à 160 °C (Figure 0.3). Wang et al. [13], qui a effectué une étude de voltoampérométrie cyclique inverse de l'EOR à plusieurs concentrations d'éthanol dans 0,5 M H₂SO₄ sur 20 % Pt/C a enregistré une moyenne d'efficacité de courant de CO₂ qui diminue légèrement lorsque la température augmente; entre 7,9 % à 30 °C et 5,1 % à 60 °C avec une concentration 0,01 M dans l'éthanol. D'autres groupes ont cependant observé une augmentation de l'efficacité de CO₂ lorsque la température augmente. Sun et al. [10] ont rapporté leurs plus hauts rendements en courant de CO₂ à leur plus bas potentiel mesuré de 0,48 V entre 4,6 % à 23 °C et 45 % à 100 °C avec 0,1 M de l'éthanol et entre 5,1 % à 23 °C et 86,9 % à 100 °C avec 0,01 M d'éthanol. De même, Rao et al. [14] ont rapporté une augmentation de l'efficacité de CO₂ lorsque la température augmente, plus de 75 % à 90 °C. Andreadis et al. [15] ont rapporté des sélectivités de CO₂ entre environ 5 % à 60 °C et 15 % à 90 °C dans des expériences galvanostatiques sur catalyseurs PtRu/C avec 1 M de l'éthanol.

Compte tenu de la température élevée de la cellule de mesure, les valeurs de l'efficacité de charge de CO₂ dans cette étude sont quelque peu plus faibles que prévu. Ainsi, alors que leur augmentation significative lorsque la température augmente est en accord avec la littérature, les valeurs absolues plutôt faibles sont probablement causées par la concentration élevée d'éthanol [10,13] et/ou de la faible surface qui peut être attendu du catalyseur noir Pt par rapport au Pt supporté par du carbone [14].
Figure 0.3: L'efficacité de la formation de CO$_2$ sur le catalyseur noir de Pt en dépendance de la température.

Un graphique d'Arrhenius de la valeur du courant au potentiel de retour supérieur de 1,1 V donne une énergie d'activation apparente de $E_A = (14,7 \pm 2,4)$ kJ/mol. Wang et al. $^{[13]}$ ont rapporté une énergie d'activation de 32 kJ/mol pour la réaction globale de 0,01 M éthanol dans la plage de température de 30 à 60 °C. Cette valeur a été déterminée par l'intermédiaire de charges intégrées mesurées pendant l'avoltamétrie cyclique. Des énergies d'activation apparentes encore plus élevées ont été signalées par Sun et al. $^{[10]}$, de 40 à 50 kJ/mol en fonction du potentiel appliqué dans leurs mesures chronoampérométriques (mesurées à 0,48, 0,58 et 0,68 V) dans la gamme de température comprise entre 23 et 100 °C sur 20 % Pt/C. Ils ont utilisé deux concentrations d'éthanol différentes, 0,01 M et 0,1 M, et ont trouvé des énergies d'activation apparentes légèrement supérieures à la concentration inférieure. Des mesures à l'état stationnaire dans une DEFC ont été publiées par Rao et al. $^{[14]}$ qui font état d'une énergie d'activation apparente de 31 kJ/mol à 0,1 M éthanol et 0,6 V sur un catalyseur à 40 % de Pt/C dans la plage de températures
entre 30 à 90 °C, ainsi que par Colmati et al.\textsuperscript{[16]} qui a rapporté 26 kJ/mol à 1 M éthanol et 0,45 et 0,55 V sur un catalyseur 20 % Pt/C compris entre 70 et 100 ° C.

Bien que les énergies d'activation apparentes déterminées par des mesures potentiostatiques et potentiodynamiques soient pas directement comparables, il semble y avoir une tendance claire vers une énergie d'activation apparente inférieure pour l'EOR totale à des concentrations d'éthanol plus élevées. Donc, l'énergie d'activation apparente basse constatée dans cette étude pourrait être causée par la concentration d'éthanol élevée. Cependant, la variation des conditions de transport de masse dans différents dispositifs expérimentaux peut avoir une grande influence sur la contribution des différentes voies de réaction et donc sur l'énergie d'activation apparente totale\textsuperscript{[10]}. Ainsi une autre explication pourrait être simplement une contribution élevée de produits secondaires produits par des voies avec une barrière d'activation basse sur le catalyseur noir de platine, ce qui est également apparent dans les MSCVs.

La plage de température plus élevée de ces mesures peut aussi être une explication possible à la différence de l'énergie d'activation apparente, car une température élevée peut influer sur la contribution des différentes voies réactionnelles. Cependant, une étude réalisée par Shimada et al.\textsuperscript{[17]} dans une DEFC avec CsH\textsubscript{2}PO\textsubscript{4} comme électrolyte solide dans la gamme de température de 235 à 260 ° C a rapporté une énergie d'activation apparente totale élevée pour l'EOR d'environ 60 kJ/mol.

\textbf{Effet du support de carbone - comparaison des catalysateurs noir de platine et Pt/C}

Une comparaison de GDE avec le catalyseur noir de platine et le catalyseur supporté de carbone sous azote à 150 °C (Figure 0.4) révèle une formation semblable de CO\textsubscript{2} provenant de la corrosion du carbone dans la région autour de 0,6 V dans le balayage anodique. Ce pic peut être relié à l'oxydation des espèces pré-adsorbé sur la surface du catalyseur, car il apparaît à un potentiel semblable à celui du pic d'oxydation du CO. Toutefois, lorsque le support de carbone est présent, une formation de CO\textsubscript{2} plus distinette peut être détectée, commençant à des potentiels inférieurs. Cela est probablement dû à la plus grande surface du support par rapport aux fibres GDL. Dans tous les cas, le maximum du courant d'ions pour m/z = 44 semble apparaître autour de 100 mV dans le balayage cathodique.
Figure 0.4: Mesures CV et MSCV (m/z = 44) sur le catalyseur noir de Pt (a, b) Pt supporté de carbone (c, d) sous azote à 150 °C (vitesse de balayage 10 mV/s).

Comme ce fut le cas pour le catalyseur noir de platine, l'oxydation de 10,9 M éthanol sur le catalyseur Pt supporté de carbone à 150 °C montrent une relation approximativement linéaire du courant et du potentiel. Diverses études DEMS ont été menées sur l’oxydation d’éthanol sur platine [7–10,12,14,18–24]. En général, la CV montre deux pics d'oxydation, un au potentiel de 0,8 V [7,8,10–12,25], et le second autour de 1,3 V [7,11,12]. La diminution du courant à des potentiels d'environ 0,8 V est généralement attribué à un blocage partiel de la surface avec de l'oxyde de Pt [10].

Sous certaines conditions toutefois, le maximum du premier pic d'oxydation est déplacé vers un potentiel plus élevé et une relation linéaire entre le courant et le potentiel a été signalée jusqu'à des potentiels de 0,8 V [8,20,21], 0,9 V [18] ou même 1,0 V [22]. Rao et al. [14,26] ont mesuré des courbes CV similaires à celles présentées ci-dessus dans un dispositif expérimental de pile à combustible Nafion® [14] et AEM [26] fonctionnant en demi-cellule. Dans le cas de la pile à combustible Nafion®, une courbe CV linéaire a pu être observée à 1 M éthanol, tandis qu’à 0,1 M éthanol la courbe CV présente un pic d'oxydation, au potentiel autour de 0,8 V. Une courbe CV quasi-linéaire a également été rapportée sur Pt dans 0,1 M éthanol dans 0,1 M KOH jusqu’à un potentiel de 1,1 V [23].
Une analyse qualitative des MSCVs indique que des quantités importantes d'acétaldéhyde sont formées sur le catalyseur Noir de platine, mais pas sur le catalyseur Pt supporté de carbone. Dans les deux cas l'acétate d'éthyle est formé comme un produit principal avec le CO₂. Une raison pour cela est la dispersion et la surface électrochimiquement active plus élevées du catalyseur Pt/C par rapport au catalyseur noir de platine. Rao et al. [14] ont rapporté des efficacités de courant inférieures pour les catalyseurs ayant une surface électrochimiquement active plus petite, mais aussi pour les catalyseurs Pt non supportés de même surface électrochimiquement active que les catalyseurs Pt supportés. Ils l’ont expliqué comme l'effet d'un temps de séjour de l'éthanol plus long au-dessus de la surface du catalyseur dans la couche de catalyseur la plus épaisse des catalyseurs supportés, par conséquence la probabilité pour l'acétaldéhyde d’être oxydé en CO₂ ou en acétate d'éthyle et acide acétique est plus élevée. De cette façon, la structure du catalyseur plus volumineux peut avoir un effet similaire à un débit plus lent [10] car ces deux influencent le transport de masse du réactif.

**Effet de la concentration d'éthanol**

Les courbes CV mesurées sur le catalyseur Pt/C avec 1 M éthanol montrent le pic d'oxydation habituellement présent dans les courbes CV de l'EOR causé par l’oxydation et l'inactivation de la surface Pt à hauts potentiels (Figure 0.5). Une comparaison qualitative des MSCVs à celles mesurées avec 10,9 M éthanol donne à penser qu’aux concentrations plus faibles plus de CO₂ et moins de produits secondaires sont formés lors de l’EOR par rapport aux concentrations élevée. Ceci est en accord avec les résultats de la littérature [10,13,14,27,28].
Figure 0.5: Mesures CV sur 10 % Pt/C, 1 et 5 M de l'éthanol, vitesse de balayage 10 mV/s.

Des mesures CV à trois concentrations d'éthanol différentes sur catalyseur PtRh/C (Figure 0.6) montrent que la forme linéaire de la courbe de CV observée à des concentrations d'éthanol élevées est un effet d'un déplacement du pic d'oxydation à un potentiel plus élevé à ces fortes concentrations. Si la limite supérieure de potentiel est élevée, un pic d'oxydation peut être observé aux concentrations d'éthanol aussi élevées que 7 M. Dans la gamme observée de 3 à 7 M il semble exister une relations linéaire entre les potentiels des caractéristiques de la courbe de CV et la concentration d'éthanol.
Figure 0.6: Mesures CV sur 7.35 % PtRh/C, 3, 5, and 7 M de l'éthanol, vitesse de balayage 5 mV/s.

**Effet de l'addition de Rh au catalyseur Pt/C**

L'EOR sur les catalyseurs Pt et PtRh supporté de carbone a été étudiée par des mesures chronoamperométriques à trois concentrations différentes d'éthanol, 1 M, 5 M, et 10,9 M à 150 °C (Figure 0.7). On a trouvé qu'en général, la meilleure performance est obtenue à une concentration en éthanol d'environ 5 M.

Sur le catalyseur PtRh/C la concentration d'éthanol a une influence plus forte sur la performance, avec la plus haute performance et la plus stable à une concentration de 5 M. Sur le catalyseur de Pt/C une performance similaire est obtenue pour toutes les concentrations de l'éthanol jusqu'à un potentiel de 0,6 V. La meilleure performance est réalisée au potentiel mesuré le plus haut (0,8V) en utilisant 10,9 M éthanol, bien que la performance à une concentration de 5 M soit comparable et semble être plus stable.
Les deux catalyseurs montrent une activité négligeable à 0,2 V, et une activité faible, mais stable à 0,4 V. L'addition de Rh au catalyseur Pt n’est pas toujours avantageux, mais semble mener à une augmentation des performances dans les conditions de hauts potentiels et de concentrations d'éthanol faibles.

A des potentiels plus élevés mesurés à 0,6 et 0,8 V une activité accrue peut être observée sur PtRh/C par rapport au Pt/C à 5 M éthanol. A 1 M éthanol et un potentiel de 0,8 V (et dans une moindre mesure à 0,6 V) le courant est instable. Cela pourrait être dû à la couverture d'oxyde élevée à la surface du catalyseur ou à l'épuisement de l'éthanol à l'anode.

A la concentration d’éthanol la plus élevée de 10,9 M les charges intégrées des courants ioniques pour m/z = 22 et 44 montrent la formation d'acétaldéhyde. L'écart entre les charges pour les deux rapports masse sur charge est plus grand sur PtRh/C que sur Pt/C et survient à des potentiels inférieurs. Apparemment, si le rapport éthanol/eau est décalé vers l'éthanol, l'effet négatif de moins de sites d'adsorption disponibles à la surface de Pt prédomine sur l'effet positif du don d'oxyde de la Rh.

Comme la formation d'acétaldéhyde, la formation de l'acétate d'éthyle est fortement influencée par la concentration de l'éthanol, avec une faible formation de l'acétate d'éthyle à 1 M éthanol et la formation de quantités significatives à 10,9 M. Là encore, la formation du produit secondaire observé sur le catalyseur PtRh/C est supérieure à celle sur le catalyseur Pt/C, en particulier à haut potentiel. Lorsque l’on compare la formation de l'acétate d'éthyle à des concentrations différentes, il doit être gardé à l'esprit que la concentration d'éthanol plus élevée conduit probablement à une augmentation de la formation de l'acétate d'éthyle à la place d'acide acétique. Puisque l'acide acétique n’est pas détecté, il est possible que la quantité totale d'acide acétique et de l'acétate d'éthyle produite ne soit pas aussi fortement influencée par la concentration en éthanol.
Figure 0.7: Densités de courant (par surface d'électrode géométrique) corrigées pour la charge de catalyseur (métal) de la GDE sur le catalyseur PtRh/C (a, c, e) et Pt/C (b, d, f) mesurés à des concentrations de l'éthanol 10,9 M (a, b), 5 M (c, d), 1 M (e, f) après un saut de potentiel de 0,14 V à un potentiel donné dans la légende.

Conclusions

Dans le travail décrit dans cette thèse, une installation expérimentale demi-cellule a été conçue pour étudier la réaction d'oxydation de l'éthanol à des températures élevées de 120 à 180 °C. Elle offre la possibilité de simuler les conditions dans DEFCS HT-PEM sur des électrodes de diffusion de gaz, en particulier l'effet de l'éthanol gazeux évaporé à des températures supérieures au point d'ébullition d'eau, tandis que la plupart des références de la littérature mesurent l'oxydation d'éthanol dans des solutions électrolyte aqueuses de H₂SO₄ plus diluées. Les conditions expérimentales sont plus proches de celles obtenues dans une cellule HT-PEM DEFC.
simple [14] que celles obtenues avec des cellules expérimentales en phase liquide [9,10,13,29] et peuvent être réalisées avec des quantités relativement faibles de catalyseur, membrane et matériau GDL.

Cette installation expérimentale permet de mesurer la distribution des produits dans le gaz étudié par spectrométrie de masse en ligne. Des conditions qui favorisent l'oxydation complète de l'éthanol en CO\(_2\) sont connues dans la littérature des études de l'oxydation de l'éthanol dans l'électrolyte liquide à des températures jusqu'à 100 °C. Ces tendances générales ont pu être confirmées pour l'EOR en phase gazeuse dans la gamme de température de 120 à 180 °C. L'efficacité de la formation de CO\(_2\) augmente avec:

- l'augmentation de la température [10,14,15]
- l'utilisation de catalyseur Pt supporté de carbone par rapport au noir de platine [14]
- la diminution de la concentration d'éthanol [8,10,14,27]
- le choix d'un faible potentiel de l'électrode [10]

En plus du choix des conditions de réaction, l'addition de Rh à l'électrocatalyseur Pt a été étudié. Des résultats précédents de Bach Delpeuch et al. ont confirmé que l'addition de Rh favorise l'oxydation complète de l'éthanol à température ambiante dans la solution H\(_2\)SO\(_4\) diluée [30,31]. Toutefois, dans la présente étude, les effets du Rh sur la distribution des produits ne sont pas concluants et un effet positif sur le rendement global a été trouvé principalement à des potentiels au-dessus de 0,4 V. Il est possible que le Rh soit rendu inerte par l'adsorption de phosphate comme il a été montré pour Ru dans une DMFC à base d'acide phosphorique [32].

En conclusion, le travail décrit dans cette thèse offre un nouvel aperçu de l'EOR dans des conditions HT-PEMFC. Il a été trouvé que l'effet positif d'une augmentation de la température qui a été prédite sur la base de mesures d'oxydation de l'éthanol dissous dans les solutions d'électrolyte aqueuses d'acide sulfurique peut être freinée par les effets négatifs sur l'activité et la sélectivité du catalyseur causés par l'adsorption de phosphate dans l'électrolyte de l'acide phosphorique concentré. Néanmoins des efficacités élevées pour la formation de CO\(_2\) pourraient être atteintes à 150 °C en choisissant une concentration d'éthanol moyenne de 5 M, un catalyseur supporté de carbone et un faible potentiel de l'ordre de 0,4 V.


1. Introduction

1.1 Fuel Cells

1.1.1 Principle of operation

Fuel Cells (FCs) are electrochemical devices that convert chemical energy to electrical energy. For this purpose, the reduction and oxidation reactions as part of a redox reaction take place in different compartments (cf. Figure 1.1). At the anode the oxidation reaction takes place, generating protons and electrons from hydrogen. The electrons flow from the anode to the cathode side via an electrical circuit with an electronic load. At the cathode electrons are consumed during the oxygen reduction reaction.

The reactant at the cathode is usually oxygen, either pure or from air. The use of pure oxygen increases the performance of the fuel cell compared to oxygen from air due to the higher partial pressure at the cathode \[1\]. While atmospheric oxygen has the big advantage of free availability, especially in cities the air can contain pollutants, like \(\text{SO}_2\) and \(\text{CO}\), that can act as catalyst poisons in low and medium temperature fuel cell systems. In the case of alkaline fuel cells even \(\text{CO}_2\), which is otherwise inert, can have negative effects as it reacts with the concentrated hydroxide and precipitates as carbonate salt. The slow kinetics and high overpotential of the oxygen reduction reaction (ORR) in acidic media are still under evaluation in terms of optimizing fuel cells operation \[2-4\].

At the anode, the occurring reaction will depend on the fuel selected. For the moment the kinetically best understood and technically most mature reaction is the hydrogen oxidation reaction (HOR). In high temperature FCs of the solid oxide or molten carbonate type, natural gas can be used instead of pure hydrogen. Though the saturated hydrocarbons in natural gas have a low electrochemical activity themselves, they undergo steam reformation to hydrogen at high enough temperatures (above \textit{ca.} \(700\) °C). For an application at lower temperatures there are other alternative fuels on their progress to practical application. While only methanol and hydrazine have been successfully implemented to date in low temperature FCs, ethanol is another potential fuel \[4\].
Figure 1.1: Scheme of a hydrogen fuel cell consisting of gas diffusion layers, supported catalyst layers and electrolyte layer.

If gaseous or highly volatile reactants (like methanol) are used in a fuel cell, the reaction only takes place at the three phase boundary between the gaseous reactant, the electrolyte or membrane, and the catalytically active surface. To enhance the three-dimensional reaction zone and the diffusion of the reactant species to the electroactive sites gas diffusion electrodes (GDE) are used. They consist of an electron conductive porous material, usually carbon, which can be further optimized by hydrophobization and modification of the structure, depending on the used electrolyte and gaseous reactant.

The electrocatalyst is made up of nanoparticles of the catalytically active metal, usually Pt or Pt-based alloys. Their particle sizes vary depending on the choice of synthesis and material, but is in the range of 1-10 nm. These are dispersed on bigger carbon nanoparticles (particles sizes around 50 nm) to achieve a large active surface area with a small metal loading.
Anode and cathode are separated by an electrolyte that must be ion conductive, but have a sufficiently high electronic resistance. For practical application it is advantageous that the electrolyte is not liquid but solid, as it diminishes leakage and corrosion and is thus more convenient for incorporation in fuel cell stacks. In low temperature fuel cells, this is accomplished by using either thin ion conductive polymer membranes or binding a liquid electrolyte in a matrix.

There are several types of ion conductive membranes: proton exchange membranes (PEMs) and anion exchange membranes (AEMs) that conduct protons and hydroxyl groups respectively.

The unit composed by the GDLs, catalyst layers and electrolyte membrane is called the membrane electrode assembly (MEA) and constitutes the central part of the fuel cell. In a single fuel cell, the MEA is sandwiched between two monopolar plates that conduct the generated current. A fuel cell stack is built by stacking several MEAs and bipolar plates, thus connecting the separate single cells in a series circuit. Figure 1.2 shows a scheme of two single cells in a stack with the bipolar plates in between transparent to illustrate the flow field channels to transport the reactants to the GDEs and the possibility of internal cooling channels to control the temperature of the stack.

A battery contains a given amount of active material to react and then needs to be recharged or replaced. In contrast, a fuel cell works under continuous supply of active material (or fuel). The reaction products formed are continuously removed from the system as exhaust.

Thus fuel cells can more readily be compared to internal combustion engines in practical terms. Their advantages are that they have no moving parts and produce minimal noise, in the case of hydrogen fuel cells they emit no exhaust gases but only water, and they can reach high efficiencies, especially when their waste heat can be used.
Figure 1.2: Scheme of a fuel cell stack, alternating layers of MEAs (GDL – gas diffusion layer, C – cathode layer, E – electrolyte layer/membrane, A – anode layer) and bipolar plates.
1.1.2 Fuel cell classification

As already mentioned above, a wide range of reactants and electrolytes can be used in fuel cells. Depending on them, the optimal working temperature can be from ambient temperature up to 1000 °C. All these variables make it hard to find a universal classification system for fuel cells. Traditionally FCs are differentiated according to the nature of the electrolyte and the temperature of operation (cf. Figure 1.3).

![Figure 1.3: Scheme comparing several types of FC regarding their reactants, mobile ions, and working temperatures.](image)

High temperature molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) have a working temperature range of 600 to 1000 °C. In the medium temperature range (around 200 °C)
are the phosphoric acid fuel cells (PAFCs). Proton exchange membrane fuel cells (PEMFCs) are limited to a working temperature under 100 °C \[4\] unless the cell is pressurised to retain sufficient relative humidity environment for optimal proton conductivity of the membrane. The alkaline fuel cells (AFCs) as well are mostly operated up to 100 °C because of the evaporation of water from their aqueous electrolyte and precipitation of the respective hydroxide, and anion exchange membrane fuel cells to ca. 60 °C due to instability of current membranes beyond this temperature.

Finally, developments dating from the early 1990s allow for the use of PEMFCs at elevated temperature, giving rise to so called high temperature PEMFCs (HT-PEMFCs). Using phosphoric acid doped polybenzimidazole membranes, they combine elements from PEMFC and PAFC at working temperatures between 150 and 200 °C \[7–10\].

High temperature proton exchange membrane fuel cells (HT-PEMFCs)

While the ion conducting properties of the polymer are mainly influenced by their ionic side groups, their mechanical, thermal, and chemical stability depends on their polymer backbone and cross-linking level as well. To optimize all these properties for the desired applications a wide range of polymers and preparation techniques have been studied \[11,12\].

Nafion®, a perfluorosulfonic acid (PFSA) copolymer is well established for use in PEMFC, but cannot be used at temperatures much higher than 80 °C at atmospheric pressure, because water is lost from the membrane and its conductivity depends on its water content \[13\]. Nafion® has a glass transition temperature around 100 °C \[14\], while other more recently developed PFSA polymers, with shorter side chains than that of Nafion, have glass transition temperatures of up to 145 °C, which increases the potential range of use of such materials, provided the membrane remains sufficiently hydrated.

Alternatives for higher temperature applications are PFSA membranes modified by addition of inorganic components that enhance water retention and thus decrease dehydration. Such membranes have been synthesized and studied by Jones and Rozière \[12,15\] and Antonucci et al. \[16\] among others.

A different approach is the use of phosphoric acid doped polybenzimidazole (PBI) membranes, which have high protonic conductivity at temperatures up to 200 °C \[4,9,12,17–20\]. In addition, PBI
membranes allow less crossover of fuel to the cathode side compared to Nafion® membranes \cite{20}.

Figure 1.4 shows several structures of PBI-polymers. Ion conductivity is achieved by protonation of the basic polymer via acid doping. Because of the use of phosphoric acid as electrolyte there are some similarities with PAFC technology. Especially regarding the corrosion of the carbon support materials of electrocatalysts due to the high acid concentration and temperature relevant studies on PAFCs have been published \cite{21–24}.

![Figure 1.4: Structural formula of a) meta-PBI, b) ABPBI, and c) para-PBI \cite{25}.](image-url)

Figure 1.4: Structural formula of a) meta-PBI, b) ABPBI, and c) para-PBI \cite{25}.
1.1.3 Oxidation of small organic molecules in fuel cells

Direct oxidation of small organic molecules like methanol, ethanol, formic acid, ethylene glycol, dimethylether and hydrazine in fuel cells has gained attention in recent years. Though hydrogen is best established as fuel for FCs, there are some drawbacks in its use. While the energy content of hydrogen per weight is extremely high, the energy content per volume is low, even in liquefied form. This problem is exacerbated by the ability of hydrogen to permeate most materials and by the need to store the gas in cooled and/or pressurized vessels. Finally, the wide explosive range of hydrogen (4 to 75 % in air) leads to a high hazard potential [26]. Several small organic molecules offer a higher energy content as well as safer and easier handling. Especially short-chain alcohols are of interest, as they are more reactive in regard to electrooxidation than alkanes.

The general term for all fuel cells oxidizing alcohols is direct alcohol fuel cell (DAFC). The word ‘direct’ indicates that the organic molecule reacts directly at the fuel cell anode in contrast to fuel cells that run on hydrogen from syngas produced from organic compounds in a catalytic steam reformer preceding the fuel cell. In terms of system simplicity, a direct oxidation of organic compounds would be preferable to the use of reformers if satisfactory performance can be achieved [33].

The methanol oxidation reaction has been researched for several decades in terms of its application in DAFCs [4,27]. The mechanism of the reaction on Pt and PtRu has been extensively studied. While several additional catalysts have been evaluated, PtRu appears to be the best available anode catalyst for low temperature direct methanol fuel cell (DMFC) applications. Here a low to medium Ru content (20-60 at%) has the best performance at low potentials, while at higher potentials, high Ru contents (60-80 at%) have been found to provide a better performance [28]. Parallel reaction pathways have been identified, which often lead to the formation of formaldehyde and formic acid as side products. There are still several open questions regarding, among others, the influence of the catalyst and the temperature on the product distribution.

To achieve higher performance, operation of HT-PEMFCs with methanol has been studied. It has been found that the use of phosphoric acid doped PBI membranes is of advantage not only because of the higher operating temperature that is possible and the subsequent activation, but also because of lower methanol crossover rates which allow for higher methanol concentrations.
in the fuel cell feed\textsuperscript{[20,29–31]}. However, under these conditions García-Díaz et al. observed that the Ru in mixed PtRu catalyst is deactivated by phosphate adsorption and that pure Pt shows a better performance.\textsuperscript{[30]}

Going to higher alcohols, the higher number of C atoms generally leads to more complex mechanisms, an increased formation of unwanted side products and a formation of intermediates that can poison the electrode. All this tends to decrease the activity for the oxidation reaction\textsuperscript{[27]}. Nonetheless, at least direct ethanol and ethylene glycol (EG) fuel cells\textsuperscript{[36–43]} show performance comparable to that obtained with methanol\textsuperscript{[27,32–34]}. Another fuels of interest that is not an alcohol is dimethyl ether (DME)\textsuperscript{[44,45]}. In addition propanol has been studied for possible application\textsuperscript{[33]}.

A thermodynamic study\textsuperscript{[35]} concluded that if optimized to come close to their theoretical efficiency and under consideration of fuel production, storage and hazard, DMFCs and DEFCs can compete with hydrogen FCs at low temperature and could even prove better at elevated temperature.

Table 1.1 lists the properties of hydrogen and the most relevant organic fuels considered nowadays for DAFC and compares them to conventional fuels. While hydrogen has the highest heating value due to its low molecular weight, its volumetric energy content is the smallest, even in liquid form. The energy density of methanol and ethanol on the other hand is comparable to that of conventional liquid fuels, with ethanol having about 2/3 and methanol 1/3 the energy density of gasoline.

Comparing methanol and ethanol, the significant difference in energy content as well as the lower boiling point and wider explosive range are a disadvantage of methanol. Another aspect to consider is that ethanol in comparison to methanol is less toxic. Moreover, ethanol can be generated from bio-mass by fermentation of sugar-based biopolymers, which is already done at a large scale. Infrastructure and experience using ethanol as fuel already exists in some countries where it is used in internal combustion engines (ICE). In addition, handling and safety requirements for ethanol are similar to gasoline. Figure 1.4 shows the principle of a fuel cell working with ethanol in a DEFC. In the ideal situation ethanol is oxidized to CO$_2$ on the anode side of the FC, while at the cathode side oxygen is reduced to water.
Despite all the mentioned advantages of ethanol as a fuel, the kinetics of the ethanol oxidation reaction (EOR) are significantly slower than those of hydrogen or even methanol. It is known that high activation energy is needed to break the C-C bond of the ethanol molecule. As already mentioned above, the mechanisms for the oxidation of organic molecules are complex. During the EOR as well, diverse adsorbed species are formed as intermediates. For this reason the electrocatalytic surface on which the reaction takes places plays an important role. Under most conditions, during the EOR partly oxidized side products of ethanol, like acetaldehyde, ethyl acetate, and acetic acid, prevail over the complete oxidation to CO$_2$.

### Table 1.1: Thermodynamic data of hydrogen, DAFC fuels methanol and ethanol, and conventional fuels for comparison$^{[26]}$.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Lower heating value MJ/kg</th>
<th>Specific weight g/L</th>
<th>Energy density kJ/L</th>
<th>Boiling point / range °C</th>
<th>Ignition limit or ignition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>120</td>
<td>0.09</td>
<td>11</td>
<td>-252</td>
<td>4 - 74 vol.-%</td>
</tr>
<tr>
<td>Methanol</td>
<td>20</td>
<td>792</td>
<td>15 900</td>
<td>64.5</td>
<td>3 - 36 vol.-%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>27</td>
<td>789</td>
<td>21 300</td>
<td>78.3</td>
<td>4 - 14 vol.-%</td>
</tr>
<tr>
<td>Propane</td>
<td>46.3</td>
<td>2.01</td>
<td>93</td>
<td>-42</td>
<td>2.1 - 9.5 vol.-%</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>44</td>
<td>0.81</td>
<td>36</td>
<td>-162</td>
<td>5 - 13.5 vol.-%</td>
</tr>
<tr>
<td>Gasoline (Octane)</td>
<td>44.2</td>
<td>720</td>
<td>31 800</td>
<td>30 - 215</td>
<td>220 °C</td>
</tr>
<tr>
<td>Fuel Oil (Decane)</td>
<td>4.6</td>
<td>830</td>
<td>35 360</td>
<td>170 - 390</td>
<td>240 °C</td>
</tr>
</tbody>
</table>
Figure 1.5: Reactions in a direct ethanol fuel cell with proton exchange membrane \[^{[46]}\].
1.2 Differential electrochemical mass spectrometry (DEMS)

1.2.1 Standard or ambient temperature DEMS

Differential electrochemical mass spectrometry (DEMS) is an analytical method for the qualitative and quantitative identification of products and intermediates involved in electrochemical reactions. To this end the electrochemical measurement is coupled with a mass spectrometer (MS). The ion currents acquired by the MS over time are then correlated with the current responses of the electrochemical measurement.

The advantage of mass spectrometry as an analytical tool is its comparatively high sensitivity. A mass spectrometer consists of an ion source, a mass selector and a detector under vacuum. Chemical compounds must enter the mass spectrometer in gaseous form. The incoming molecules or atoms are ionized in the ion source. The resulting ions are characteristic for the chemical compound and the kind of ion source used. After the ionization, mass selection takes place. In a quadrupole mass filter the incoming ions are subjected to an oscillating electrical field in between four parallel rods. The path of passing ions can thus be selectively stabilized or destabilized depending on their mass and charge. As a result only ions of a certain mass to charge ratio are detected at a given frequency of the electrical field. These are finally detected, usually in an electron multiplier.

Mass spectroscopy had long been used as an analytical tool for detection and identification of chemical compounds, usually by analyzing the gas phase over a compound or its vapour. In contrast to many spectroscopic methods, the destruction of the sample in the MS leads to a certain disadvantage for in situ measurements. In cases where a continuous and fast sampling from a matrix should be achieved, the interface between the matrix and the MS is critical. In the early 1960s the concept of membrane introduction to conduct MS measurements (MIMS) was introduced by Hoch and Kok \[47\]. Different membrane materials can be used with this method to selectively detect only specific compounds \[48\].

Bruckenstein and Gadde \[49\] were the first to implement this technique for the evaluation of electrochemical reactions. They detected gaseous electrochemical reaction products \textit{via} MS by placing a PTFE membrane between a porous electrode and the vacuum system of a MS. Volatile
reaction products permeated through the membrane to be detected without the interference of their aqueous environment.

In the 1980s Wolter and Heitbaum \cite{50} established differential electrochemical mass spectrometry (DEMS) as an analytical tool. They developed a set-up with a significantly reduced delay time between the electrochemical formation of a compound and its detection in the MS. The term ‘differential’ was used in order to distinguish this time- and potential- resolved correlation of the mass ion and electrode current from unresolved methods.

PTFE membranes are widely used for DEMS applications because of the rapid response time and low selectivity \cite{48}. Using the flexibility of these membranes, the use of MS was adapted to different electrochemical applications \cite{49,51–54}.

DEMS facilitates not only the detection of reaction products in continuous electrochemical reactions, but can also be used to detect adsorbates on the electrode surface after their electrochemically induced desorption \cite{55}. These so called stripping experiments can yield information on the nature of adsorbed intermediates of electrochemical reactions as well as on the properties of the electrode surface.

The design of a DEMS cell depends on the electrode material or reaction studied as well as the desired conditions concerning the electrolyte and its flow. Several set-ups have been presented \cite{55}.

Several EOR products can be detected via MS (Table 1.2). The mass spectrometric ion current for mass to charge ratio \(m/z = 22\) corresponds to the \([CO_2]^{2+}\) fragment of CO\(_2\). An analysis of the other mass spectrometric signals is less straightforward since the signals for \(m/z = 44\) and 29 can be assigned to more than one oxidation product. While acetaldehyde has two major fragments – \([CH_3-CHO]^+\) and \([CHO]^+\) – with the mass to charge ratio 44 and 29 respectively, the carbon dioxide fragment \([CO_2]^+\) also has \(m/z = 44\). Ethyl acetate, the esterification product of acetic acid and ethanol (cf. Chapter 1.2.4), corresponds to \(m/z = 61\) but can also contribute to \(m/z = 29\) \cite{56}.

The signal \(m/z = 15\) can be used in stripping experiments to detect reductive formation of methane from organic adsorbates on the catalyst surface in cathodic scans \cite{59}. In an anodic scan or for bulk oxidation the signal cannot be assigned to a single compound as it can be caused by ethanol as well as any of its oxidation products containing a methyl group.
Table 1.2: Mass to charge ratio of ion current signals corresponding to compounds relevant for the study of the EOR.

<table>
<thead>
<tr>
<th>m/z signal</th>
<th>Molecules</th>
<th>Formula</th>
<th>Detected ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Hydrogen</td>
<td>H₂</td>
<td>[H₂]⁺</td>
</tr>
<tr>
<td>15</td>
<td>Methane, (methyl group)</td>
<td>CH₄</td>
<td>[CH₃]⁺</td>
</tr>
<tr>
<td>22</td>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>[CO₂]²⁺</td>
</tr>
<tr>
<td>29</td>
<td>Ethanol, acetaldehyde</td>
<td>CH₃-CH₂OH, CH₃-CHO</td>
<td>[CH₃]⁺</td>
</tr>
<tr>
<td>44</td>
<td>Ethanol, acetaldehyde, carbon dioxide</td>
<td>CH₃-CH₂OH, CH₃-CHO, CO₂</td>
<td>[CH₃-CHO]⁺, [CO₂]⁺</td>
</tr>
<tr>
<td>60</td>
<td>Acetic acid</td>
<td>CH₃-COOH</td>
<td>[CH₃-COOH]⁺</td>
</tr>
<tr>
<td>61</td>
<td>Ethyl acetate</td>
<td>CH₃-COO-CH₂-CH₃</td>
<td>[CH₃-CH₂-OO]⁺</td>
</tr>
</tbody>
</table>
1.2.2 DEMS at elevated temperature / HT-DEMS

The established DEMS set-up can differ, as described above, but generally uses a liquid aqueous electrolyte as matrix. This and the PTFE membrane interface to the MS limit the set-up to temperatures up to around 100 °C.

DEMS is an appropriate and well-established analytical method to study the product distribution in DAFC anode reactions \[^{36,60-63}\]. There is an interest in studying these reactions at elevated temperature because reaction kinetics are expected to be improved.

A pressurized high temperature DEMS set-up was developed by Sun et al. \[^{64}\] to study the product distribution in DAFC anode reactions by conducting liquid phase measurements at temperatures up to 100 °C. On-line mass spectrometric investigations of the product distribution in the exhaust of HT-PEMFC single cells were conducted at temperatures above 100 °C (cf. Chapter 1.1.2). However, no DEMS measurement has been conducted in the gas phase using a half cell set-up yet.

In view of implementing mass spectrometry to detect the species involved in DAFC reactions, in the scope of this work a set-up has been developed to carry out DEMS measurements on model electrodes under HT-PEMFC conditions.
1.2.3 Antecedents on the evaluation of the EOR

The electrooxidation of ethanol on platinum has been studied for its application in the DEFC on the one hand and for the development of electrochemical sensors on the other hand. In addition, it is of interest as a model system for electrocatalysis \cite{65}. Relevant knowledge has been gained on the intermediate adsorbates during the EOR by studies of the electrooxidation of ethanol itself as well as other compounds, especially methanol and its oxidation products as well as acetaldehyde, acetic acid, and CO \cite{66}.

Several methods have been applied and combined to evaluate the kinetics of the EOR. Especially since the 1980s significant progress has been made in the understanding of the surface reactions taking place during the electrooxidation of small organic molecules. This was in a large part due to the development and improvement of two important experimental methods which have been applied in combination with electrochemical methods: \textit{in situ} Fourier transform infrared (FTIR) spectroscopy and on-line mass spectrometry (MS). MS is often combined with isotope labelling, \textit{e.g.} to differentiate between CO$_2$ formed from the methyl and alcohol group C atom of the ethanol molecule.

In addition, several \textit{ex situ} techniques have been used to identify reaction products formed on the electrodes. These include chromatography and IR absorbance measurements, as well as surface sensitive techniques like X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and X-ray diffraction (XRD) \cite{66}.

Some relevant infrared (IR) spectroscopic techniques applied for the evaluation of the EOR are electrochemically modulated IR spectroscopy (EMIRS), IR reflection-absorption spectroscopy (IRRAS), and subtractively normalized interfacial Fourier transform IR spectroscopy (SNIFTIRS). In all these techniques the IR beam is reflected off the surface of a mirror smooth electrode in solution. To measure the spectra of the species adsorbed in a sub-monolayer on the electrode over the absorption of the species in the surrounding aqueous bulk solution, the solvent absorption has to be subtracted out and the sensitivity for the adsorbed species has to be increased. To distinguish between surface and bulk species in EMIRS the electrode is modulated between two limiting potentials, while in IRRAS the polarization of the incident light is
modulated instead. Using SNIFTIRS information on the orientation of the adsorbates relative to the surface can be obtained.

The following paragraph gives a résumé of previous work done on the EOR in acidic media. Unless noted otherwise the studies were performed at ambient temperature and in a three-electrode assembly.

Willsau and Heitbaum\textsuperscript{[67]} carried out differential electrochemical mass spectrometry (DEMS) studies on isotope labelled 0.01 M ethanol on a porous Pt catalyst consisting of smooth particles of 5µm mean size. They observed two parallel reaction pathways, one leading to acetaldehyde \textit{via} a weakly adsorbed intermediate at potentials as low as 0.3 V, while the other led to two molecules of CO\textsubscript{2} \textit{via} a strongly adsorbed intermediate. They could prove that both the methyl and alcoholic group are oxidized to form CO\textsubscript{2} at a potential around 0.7 V and connected it to the onset of the oxide formation on the Pt surface.

Using EMIRS Beden \textit{et al.}\textsuperscript{[68]} studied the species formed by adsorption of 0.1 M ethanol in 0.5 M HClO\textsubscript{4} on smooth Pt, and found that, depending on the potential conditions, upon ethanol adsorption the Pt surface is almost entirely covered by linearly and multi-bonded adsorbed CO, with only a small amount of coexisting species. They could not confirm the existence of an acetyl adsorbate, which had been suggested by Willsau and Heitbaum as an intermediate in the oxidation of ethanol to acetaldehyde. They instead suggested a bridge-bonded [\text{\textasciitilde}CO-\text{CH\textsubscript{3}}]\textit{ species as an intermediate.}

Another study focusing on the intermediate adsorbates of the EOR in acidic solution was published by Bittins-Cattaneo \textit{et al.}\textsuperscript{[69]} using IRRAS, DEMS and electrochemical thermal desorption mass spectrometry (ECTDMS). Here also, isotope labelled ethanol was used to distinguish between the oxidation products of the alcoholic and methyl group. These results confirmed that the bulk oxidation of 0.01 M ethanol in 0.05 M H\textsubscript{2}SO\textsubscript{4} at a smooth Pt electrode yielded acetaldehyde and CO\textsubscript{2} as the main products while methane could be detected at low potential (< 0.2 V\textsuperscript{[70]}). In agreement with Beden \textit{et al.} the adsorbates were identified as being mainly CO\textsubscript{ad} and COH\textsubscript{ad} (at 0.4 V), but a small amount of C\textsubscript{2} adsorbates could be detected as well. Concerning the structure of these C\textsubscript{2} adsorbates they ruled out the acetyl adsorbate suggested by Willsau and Heitbaum, as well as the ethoxy adsorbates suggested by Beden \textit{et al.}
Several studies on the reaction products, intermediates and mechanism of the EOR were performed by Iwasita \textit{et al.} [65,70–72] using SNIFTIRS at different electrode potentials and ethanol concentrations in 0.1 M HClO$_4$ solution [65]. The results showed that on smooth polycrystalline Pt, linearly adsorbed CO was the only surface species detected. The observed products of the bulk oxidation were acetaldehyde, CO$_2$ and acetic acid. Though existence of the C$_2$ products necessitates the existence of C$_2$ adsorbates, they could not be detected probably due to being masked by the bulk species. Also these authors found that at low ethanol concentration CO$_2$ and acetic acid were formed, while a high ethanol concentration favoured the production of acetaldehyde. This was explained by a poisoning effect of the ethanol adsorbates at high ethanol concentration leading to a lack of OH$_{ad}$ required for the formation of CO$_2$ and acetic acid. The possibility of ethyl acetate formation in the bulk was discussed in this publication, but could not be proven.

In their later work Iwasita \textit{et al.} [70,71] were able to identify three different C$_2$ adsorbates on smooth Pt using \textit{in situ} FTIRS, DEMS and ECTDMS. In contrast to the results by Bittins-Cattaneo \textit{et al.} significant amounts of C$_2$ could be detected at potentials of 0.30-0.35 V. These are (i) a bridge bonded [=COH-CH$_3$] species similar to the one suggested by Beden \textit{et al.} (ii) an ethoxy species [-OCH$_2$-CH$_3$], in disagreement with Beden \textit{et al.} who ruled it out based on not observing any absorption by the methyl group (iii) an acetyl species [-CO-CH$_3$] in agreement with Willsau and Heitbaum and disagreement with Beden \textit{et al.}

Iwasita \textit{et al.} concluded that in absence of ethanol in the electrolyte all of these adsorbates are oxidized to form only CO$_2$. They theorized that the intermediate leading to acetaldehyde might not be bound directly to a Pt site, but reacts with an adsorbed water or hydroxide molecule.

A mechanism for the surface reactions during the EOR on smooth Pt in acidic medium was proposed by Hitmi \textit{et al.} [73]. This mechanism proposes the adsorption of ethanol via dehydrogenation of the alcoholic C atom to form adsorbed [–CHOH-CH$_3$] as an intermediate for the acetaldehyde formation. Other intermediates suggested by this mechanism are an adsorbed [-CH$_2$-CH$_3$] species that is oxidized stepwise. The first step is a bridge bonded [=COH-CH$_3$] intermediate (in agreement with Iwasita \textit{et al.} and Beden \textit{et al.}) and the second an adsorbed acetyl species [–CO-CH$_3$] (in agreement with Willsau and Heitbaum) as precursor for further oxidation to either acetic acid or CO$_2$ via CO$_{ad}$. The mechanism does not detail the C-C bond scission or the
oxidation of the methyl carbon to form $\text{CO}_2$ (as proven to occur by measurements using isotope labelled ethanol $^{[67,69]}$).

A partially contradictory mechanism has been suggested Lai and Koper $^{[74]}$. They suggest a bidentate acetate adsorbate (-$\text{O-CCH}_3\text{-O-}$) as an intermediate in the formation of acetic acid. They also implicated the adsorption of ethanol via the O atom forming ethoxy adsorbates.

As can be seen, there seems to be no general consensus in the literature regarding the adsorbed intermediates of the EOR. Several possible intermediates have been proposed or rejected mainly based on IR measurements of adsorbates on smooth Pt surfaces.

Another very important method to obtain information of the EOR intermediates and products is the use of computational theory. Using infrared-visible sum frequency generation (SFG) spectroscopy in combination with density functional theory (DFT) calculations, Gomes et al. $^{[75]}$ found evidence for the co-existence of several different adsorbed intermediates. They were able to confirm the existence of most of the adsorbates proposed by other authors as well as additional ones, suggesting that the reaction mechanism of the EOR might be even more complex than previously considered.

In order to study the EOR over carbon supported Pt, like the electrodes used in fuel cells, MS is a valuable analytical tool. Several studies were made on the EOR on carbon supported Pt as well as on the effect of adding other transition metals to the Pt catalyst $^{[62,64,76–80]}$ (cf. Chapter 1.2.5). As they can gain no direct information on the adsorbates, these MS studies focus on the product distribution of the EOR and how they are influenced by different experimental conditions.

Wang et al. $^{[33]}$ used on-line MS to evaluate ethanol and propanol for use in fuel cells, determining their performance and product distribution under HT-PEMFC conditions at 170 °C. The electrooxidation of ethanol, ethylene glycol and n-propanol was evaluated by Lamy et al. $^{[32]}$ at room temperature and 145 °C. Both came to the conclusion that ethanol is a promising fuel for a direct alcohol fuel cell with performances comparable to methanol. During oxidation under HT-PEMFC conditions however, significant amounts of side products are formed. In this regard, it was determined that the product distribution is very sensitive to the experimental conditions. While Wang et al. found acetaldehyde to be a main product besides $\text{CO}_2$, Lamy et al. detected only small amounts of $\text{CO}_2$ with acetic acid and acetaldehyde being the main products.
Several DEMS studies have been done in order to detect the products formed during the EOR on carbon supported catalysts in test cells as well as fuel cell set-ups. While a lot of them were carried out on samples in acidic medium \[39,43,79,81\], some work has been done in alkaline medium \[57,59,82,83\] which has the advantages that non-noble metal catalysts can be used and that the reaction kinetics of ORR (as the cathode reaction in single cells and stacks) as well as the oxidation of organic species are faster \[82\].

For the EOR in acidic medium, Rao \textit{et al.} \[81\] published a study based on DEMS measurements of the exhaust of a fuel cell at 30, 60 and 90 °C. They found the selectivity for CO\textsubscript{2} formation increased with increasing temperature and catalyst loading and thickness, and decreasing ethanol concentration (in the range of 0.01 to 1 M) and anolyte flow rate. A high potential (> 0.6 V) also led to a decreasing CO\textsubscript{2} production.

Sun \textit{et al.} \[39,43,64,84\] built a pressurized DEMS test cell to evaluate the EOR at high temperature. With this set-up they were able to measure in liquid electrolyte at elevated temperature up to 100 °C. Their measurements of the CO\textsubscript{2} selectivity agree with the general trends mentioned above. In addition they conclude that according to their measurements the rate limiting reaction steps for the overall EOR as well as the CO\textsubscript{2} formation do not change with temperature in the range of 23-100 °C.
1.2.4 Mechanism of the EOR

The mechanism of the electrochemical oxidation of ethanol on Pt is not completely resolved. There is no disagreement that under most experimental conditions, incomplete oxidation products are formed besides CO$_2$. These incomplete oxidation products are mainly acetaldehyde and acetic acid [84–87]. Taking into account this evidence, the mechanism of the electrochemical oxidation of ethanol can be considered to follow three different reaction pathways:

1) Partial oxidation of ethanol to acetaldehyde

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-
\]

Equation 1.1

The formation of acetaldehyde was observed as a main product besides CO$_2$ in most measurements of ethanol bulk oxidation on Pt [60,62,72,79,88]. Compared to the other oxidation reactions, the mechanism of this reaction should be fairly simple, as no oxide species is needed as a second reactant. However, the nature of the adsorbed intermediate(s) leading to acetaldehyde has caused some controversy in literature (cf. Chapter 1.2.3).

2) Partial oxidation of ethanol to acetic acid

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^-
\]

Equation 1.2

It has been suggested that acetic acid can be formed in a pathway containing only adsorbed intermediates as well as a pathway including the readsorption and oxidation of previously formed acetaldehyde (cf. Equation 1.1) [73]. The acetaldehyde oxidation reaction is known to form acetic acid and CO$_2$ as reaction products [84,85,87,89–91]. It has been shown that further oxidation of acetic acid to CO$_2$ on Pt occurs at temperatures of 200 °C and higher in an autoclave electrochemical cell [92]. Nonetheless, the reaction rate is negligible under the relevant experimental conditions [84]. Thus, acetic acid can be considered a dead-end side product in the low to medium temperature range [81].
Ethyl acetate, the ester of acetic acid and ethanol, is formed as well \[33,60,62\]. Because of its higher volatility it is often more easily detected by MS methods than the acetic acid itself. Concerning the formation, Bayer et al. \[57\] found that the esterification occurs only at the catalyst surface in aqueous alkaline media. Abd-El-Latif et al. \[58\] studied the esterification of methanol and formic acid in acidic environment. He showed that, in this case as well, the formation of the ester during the surface reaction, \textit{i.e.} a nucleophilic attack of methanol instead of water on the oxidized adsorbate, is much faster than the esterification of desorbed formic acid in a follow-up reaction. It is likely that this is also the case for ethanol in acidic medium. Thus, while the formation of ethyl acetate in a follow-up reaction cannot be entirely excluded, it is likely negligible compared to the parallel formation of ethyl acetate and acetic acid on the Pt surface.

3) Complete oxidation of ethanol to carbon dioxide

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-
\]

\text{Equation 1.3}

To facilitate the complete oxidation of ethanol to CO\(_2\) the C-C bond has to be broken. On the one hand the bond scission requires a certain activation energy \[64\], on the other hand the availability of free adsorption sites seems to play an even bigger role. The adsorption of small amounts of ethanol on clean Pt surfaces has been found to yield large amounts of C\(_1\) adsorbates \[65\], and pre-adsorbed C\(_2\) species could be completely oxidized to CO\(_2\) in ethanol-free electrolyte \[71\]. These facts show that C-C bond breaking is generally feasible. During bulk oxidation though, especially at high ethanol concentration in the electrolyte, this reaction pathway seems to be hindered and acetaldehyde and acetic acid are often detected as the main products \[60,62,71,79,88\].

Small amounts of incomplete C\(_1\) oxidation products like formaldehyde and formic acid might be formed from C\(_1\) adsorbates as side products \[75\].

The first step in the ethanol oxidation is the adsorption of an ethanol molecule on the electrocatalytic platinum surface under dehydrogenation of either the –OH group or the α-carbon.

After this step, the ethoxy- or ethanol adsorbates can release further protons leading to the formation of acetyl species or to C-C bond dissociation. At this point it is not known exactly which adsorbed intermediates are involved in which reaction pathways and how their formation and reactions are influenced by experimental parameters \[75\].
Several works have been published on the temperature dependence of the EOR product distribution \cite{64,79}. Due to the thermal activation of the C-C bond splitting, a complete oxidation is favoured at elevated temperatures. According to Sun et al. complete oxidation of ethanol to CO$_2$ can only be expected at temperatures between 140 and 180 °C. At temperature of 40 °C or below, CO$_2$ is formed as a side product at best, while acetaldehyde and acetic acid are the main products of ethanol oxidation \cite{64}.

A high concentration of ethanol in the electrolyte leads to a higher ratio of incomplete reaction products due to more molecules competing for free surface sites during adsorption. Low concentrations on the other hand lead to a faster depletion of the ethanol at the electrode and thus a stronger influence of mass transport limitations on the reaction. Consequently, an optimum must be found where the performance has a maximum at high CO$_2$ current efficiency. This optimum depends on the electrode materials, but is expected to be around 0.1 M for most set-ups at room temperature \cite{72,79,81}.

Experiments regarding the oxidation of acetaldehyde and acetic acid indicate that the re-adsorption of acetaldehyde on the electrode and further reaction to acetic acid or CO$_2$ leads to a corresponding shift in the product distribution if the dwell time of the reactants over the catalyst surface is increased \cite{81}.

This makes the flow rate of the electrolyte another relevant factor, since a fuel cell works with a continuous flow. The faster the flow rate of the electrolyte, the less likely is a re-adsorption and subsequent oxidation of acetaldehyde formed. Indeed, a high flow rate has been found to heighten the amount of acetaldehyde formed while less CO$_2$ and acetic acid are produced \cite{81}.

In addition, the morphology of the Pt catalyst can have an impact on the product distribution of the EOR. The porosity and thickness of the catalyst and gas diffusion layer influence the diffusion of reactants to the catalyst surface and thus the re-adsorption of oxidation products \cite{81}.

The C$_1$ species formed during dissociation have been identified as CO$_{ad}$ and CH$_{x,ads}$, the latter of which can be oxidized to CO$_{ad}$ under stepwise deprotonation and reaction with adsorbed water species on the Pt surface (Equation 1.4).

\[
\text{CH}_{x,\text{ad}} + \text{H}_2\text{O} \rightarrow \text{CO}_{ad}^+ + (2+x)\text{H}^+ + (2+x)e^-
\]

Equation 1.4
CO_{ad} is finally oxidized to CO_{2}:

\[
\text{CO}_{ad} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-
\]  

**Equation 1.5**

The reaction in Equation 1.5 is also part of the electrochemical oxidation of CO (COOR, CO oxidation reaction). Since the COOR has been extensively researched, this part of the EOR is comparatively well understood. Numerous literature has been published, even though, Gilman was the first to propose the COOR over Pt using the Langmuir-Hinshelwood adsorption mechanism \[^4\]. In this mechanism it is considered that the electrocatalyst free sites (S) are activated through water adsorption:

\[
\text{H}_2\text{O} + \text{S} \rightleftharpoons \text{OH}_{ad} + \text{e}^- + \text{H}^+
\]  

**Equation 1.6**

In the same way CO is adsorbed on the free sites of the electrocatalyst:

\[
\text{CO} + \text{S} \rightarrow \text{CO}_{ad}
\]  

**Equation 1.7**

The \text{OH}_{ad} intermediate is the oxygen donor species that adsorbed on the proximity of \text{CO}_{ad} will promote the oxidation of the carbon adsorbate:

\[
\text{CO}_{ad} + \text{OH}_{ad} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- + 2\text{S}
\]  

**Equation 1.8**
Figure 1.6: Possible adsorbates formed during EOR on Pt\textsuperscript{[75]}.
**1.2.5 Electrocatalysts for DEFCs**

Pt is one of the metals with the highest electrocatalytic activity towards the EOR in acidic medium \[^{[93]}\]. In addition Pt is more corrosion-resistant than many other metals. However, considering its cost as well as the formation of side products and unsatisfying overall reaction rates of the EOR on Pt, other catalysts have been studied to promote the complete oxidation of ethanol to CO\(_2\).

There is a strong interest in increasing the electrocatalytic activity of the electrocatalyst for the EOR by means of a modification of the catalyst surface structure or by use of bi- or trimetallic electrocatalysts. Most of the alloy catalysts studied are platinum-based, with added transition metals. Especially ruthenium (Ru), tin (Sn) and rhodium (Rh) have been shown to have a positive influence on the product distribution or on decreasing the effects of catalyst poisoning. While in alkaline medium, Pt-free non-noble metal catalysts like nickel (Ni) have been studied \[^{[57]}\], because of their corrosion in acidic media most studies concentrate on Pt-based catalysts with one or two added transition metals.

The addition of other metals modifies the physical structure of the catalyst surface as well as its electronic nature. This way the formation of poisoning adsorbates can be avoided by either blocking their adsorption or by promoting their desorption. Here an important factor is that the ad-metal provides adsorption sites for OH\(_{ad}\) so they can react with other adsorbates \[^{[66,93]}\]. Thus, by modifying the Pt with other metals, its catalytic properties can be enhanced.

Ruthenium (Ru) has been known to cause an increase in activity for the oxidation of carbon monoxide and methanol \[^{[94]}\] by providing sites for the adsorption of OH\(_{ad}\) at lower potentials than Pt and thus promoting the oxidation reaction of the CO\(_{ad}\) formed as an intermediate in both oxidation reactions (bifunctional mechanism) \[^{[95-97]}\]. For oxidation of ethanol however, the effect of Ru is not as straightforward. It has been found to partially inhibit the adsorption of ethanol in some cases \[^{[98,99]}\], while in other cases a positive effect analogous to the methanol oxidation seems to prevail \[^{[93]}\]. It has to be mentioned that because of the large influence of the experimental parameters, especially temperature and ethanol concentration, but also anolyte flow and catalyst thickness and loading (cf. Chapter 1.2.1), it is often hard to compare measurements performed with catalysts of different composition.
Tin (Sn) actually exists as oxide SnO$_2$ on the catalyst surface as Sn is easily oxidized in contact with air or aqueous electrolyte \[^{100}\]. It appears to have a similar catalytic effect to that of Ru in that it is oxophilic and thus provides OH$_{ad}$ species at an even lower potential than Ru. It has been found to significantly improve the overall performance of DEFCs \[^{62,100–105}\], but generally seems to favour the reaction to acetic acid as the final product \[^{62,93,104,105}\].

The effect of Ru and Sn depends strongly on the amount of ad-metal present. It is assumed that while on the one hand, a high amount of Ru or Sn on the Pt surface promotes all reactions needing OH$_{ad}$, on the other hand, a too high coverage of the Pt surface with the other metal (oxides) decreases the likelihood of dissociative adsorption of the ethanol as the amount of neighbouring Pt-adsorption sites necessary for the reaction step decreases. While the overall performance of DEFCs seems to benefit from the first effect, in several cases the product distribution is shifted towards the incomplete oxidation products.

Rhodium (Rh) in contrast might actually favour the complete oxidation to CO$_2$ by promoting the C-C bond splitting. Some studies have been carried out on the oxidation of CO \[^{106–111}\] and methanol \[^{112–115}\] on PtRh/C. Tokarz \textit{et al.} found a negative shift in the onset of the CO$_{ad}$ oxidation during CO stripping experiments as well as slightly lower overpotential for the methanol oxidation compared to Pt/C \[^{112}\].

Several studies have been performed on the EOR activity of bi- and trimetallic PtRh catalysts \[^{60,63,78,116–126}\]. On its own, Rh shows a certain activity for the EOR, but it is significantly lower than that of Pt. This is explained by an insufficient ethanol adsorption at low ethanol bulk concentrations as well as poisoning by decomposition products \[^{116,127}\]. Rh has been found to support C-C cleavage \[^{128,129}\]. In PtRh catalysts, this is thought to be caused by a downshift of the Pt 5d-band centre due to the lattice interactions between Pt and Rh which decrease the adsorption strength of adsorbates, facilitating their oxidation \[^{130}\]. In addition, Rh can also supply OH$_{ad}$ at a lower potential similar to Ru and Sn, resulting in a lower EOR onset potential \[^{60,63,119,121,131}\].

DEMS measurements by Cantane \textit{et al.} \[^{60}\] suggest that the EOR on carbon-supported Rh follows the same general trends concerning the influence of temperature and ethanol concentration on the CO$_2$ yield as on Pt. According to these authors, Rh has a higher selectivity for CO$_2$ formation than Pt, which is in disagreement with the IRRAS results of Li \textit{et al.} \[^{116}\]. Apart from that Li \textit{et al.} found that while the PtRh bimetallic catalyst shows a higher activity than Rh, but a lower
activity than Pt, it shows a higher selectivity for CO$_2$ formation than either of the pure metals. In agreement with this, de Souza et al. \cite{118} as well as Bergamaski et al. \cite{63} reported that the addition of Rh to Pt significantly reduces the amount of acetaldehyde produced and increases the CO$_2$ yield, while lowering the overall activity. Lima et al. \cite{119} found a higher conversion efficiency to CO$_2$ as well as a slightly higher Faradaic current on Pt$_1$Rh$_1$/C compared to Pt/C. Similarly Gupta and Datta \cite{121} reported a higher activity for some of their Pt$_3$Rh$_1$/C and Pt$_1$Rh$_2$/C catalysts compared to Pt/C, but a lower activity for a Pt$_9$Rh$_1$/C catalyst. Bach Delpeuch et al. \cite{123} published DEMS studies on home-made Pt, Rh and PtRh catalysts and could confirm a higher performance of Pt, but a better CO$_2$ selectivity and slightly earlier onset of the EOR on PtRh.
1.3 Motivation

The electrochemical oxidation of ethanol is of interest as a model reaction on the one hand and for its potential use in direct alcohol fuel cells on the other hand. The mechanism of the reaction is not yet completely understood and the product distribution has been shown to be strongly influenced by the reaction conditions. The scission of the C-C bond in particular is of key importance for a possible application as it is the critical step for complete oxidation to CO₂. The kinetics of this reaction step can be enhanced by operating the fuel cell at elevated temperature, so the use of HT-PEMFC technology at temperatures between 120 and 200 °C is of interest for optimization of the reaction. Up to now, studies on the EOR have been conducted either in half cell set-ups working at temperatures up to 100 °C in liquid electrolyte, or with gaseous electrolyte at temperatures above 100 °C in HT-PEMFC single cells or stacks.

The aim of the work described in this thesis was the development of a half cell set-up that could measure the EOR in the gas phase at temperature between 120 and 180 °C.

The work done for this thesis was part of the project for efficient use of bio-ethanol in fuel cells (EUBECELL), a collaboration of the Instituts Carnot Energies du Futur and Chimie, Environnement et Développement Durable and the Fraunhofer Institute for Chemical Technology, and the Industrial partners Südzucker and Fumatech. This work was co-supervised by Fraunhofer ICT and the Université de Montpellier. The project was part of the Programme Inter-Carnot-Fraunhofer (PICF) financed by the French National Research Agency (ANR) and the German Federal Ministry of Education and Research (BMBF). Its objective was the study and optimization of DEFC catalysts and reaction conditions for an application in elevated temperature and alkaline fuel cells.
2 Experimental Section

2.1 DEMS set-up

A special three electrode DEMS cell was created in order to study the reactivity of small scale model electrodes under working conditions close to those in a HT-PEMFC and particularly for the evaluation of the EOR. The designed cell employs a polymer electrolyte membrane and a gas diffusion electrode (GDE) ensemble forming a half MEA of the HT-PEMFC. Moreover, taking into account the operating conditions of a conventional HT-PEMFC, the developed set-up allows for working under atmospheric pressure heating up to 180 °C and keeping the temperature stable for a long time during measurements. Under these experimental conditions the ethanol enters into the cell as preheated gas. For this reason condensation must be avoided to offer a homogenous distribution of the gases.

A mass spectrometer (MS), which is used to detect volatile products of the EOR, is connected to the three electrode cell by a heated capillary placed in the gas outlet. In this way, volatile products formed over the active surface of the working electrode can be pumped into the MS, which enables the qualification and quantification of the produced compounds by measuring their corresponding mass currents.[55]

As the model system should be as close to an actual HT-PEMFC as possible, the working electrode (WE) is a gas diffusion electrode, comprised of a catalyst layer coating on a gas diffusion layer (GDL). The GDL not only provides mechanical support for the electro-catalyst but also allows a continuous transport and distribution of the gases[132] as well as the conduction of electrons. A detailed explanation of the electrode preparation will be given in Chapter 2.1.4.

The other two electrodes used in the set-up are a counter electrode (CE), and reference electrode (RE) connected via a Luggin-Haber capillary, which allows the accurate measurement of the WE potential. Ionic conduction between the electrodes is a required condition. To achieve this, the counter and reference electrode need to be immersed in a liquid electrolyte. In contrast, in order to function, the WE must not be soaked in electrolyte, because this would prevent the gaseous reactants from reaching the catalyst layer. Thus, a separator that allows ion exchange with the electrolyte at high temperature is needed. To this purpose a polybenzimidazole (PBI) membrane
doped with phosphoric acid was employed. This type of proton exchange membrane is commonly used for the same task in HT-PEMFCs\cite{25,133–135} and also allows for the impregnation of the WE with the required amount of phosphoric acid to form three phase boundaries. Consequently, concentrated phosphoric acid was the obvious choice as electrolyte.

The material of the cell needed to be able to withstand the aggressive environment of the chemicals used (i.e. hot concentrated phosphoric acid as well as ethanol and water vapor) at high temperatures up to 200 °C. Taking this into account, the material chosen was polyether ether ketone (PEEK). This polymer is a thermoplastic that is mechanically stable up to about 250 °C and exhibits the necessary chemical resistance\cite{136}. In addition this material can be easily processed into the parts required for the set-up.
2.1.1 Electrochemical Cell design

The cell design is detailed in Figure 2.1. As is possible to see in this scheme, the cell consists of three stacked main parts: a top, a body and a bottom. In order to simplify the mounting process the cell was formed in a cylindrical shape with an outer diameter of 50 mm and a total height of ca. 100 mm.

The bottom of the cell is the most complex part. It accommodates the working electrode and the polymer electrolyte membrane. There takes place the supply of gaseous educts as well as the removal of volatile products. It is a flat cylinder (height ca. 14 mm) containing a conical chamber with a nozzle in the center (1) which ends underneath the working electrode (2) and through which the reactant gases enter. The working electrode (WE) is supported on a PEEK sieve (3) (diameter 20 mm, thickness 2 mm) with 1 mm diameter holes spaced 0.45 mm from each other in a square raster, and a hole in the middle big enough for the nozzle. The sieve is placed above the conical chamber. Between the PEEK support and the WE a thin gold mesh (4) facilitates electron conduction to the contact outside the cell. The WE is placed on top of it with the catalyst layer side up, facing the PBI membrane (5). From the conical chamber underneath, the gas outlet (6) leads outside and provides connection to the MS.

A 1/16” PEEK capillary with an inner diameter of 1 mm and a length of approximately 5 cm leads outside the cell. A heated 1/8” capillary is fitted over the 1/16” capillary. The former is connected to a 2 m heated capillary with an inner diameter of 0.25 mm which leads inside the MS. This way the 1/16” capillary coming from the cell faces the smaller capillary that leads inside the MS within the heated 1/8” outer capillary. This construction has been necessary because of the tendency of the 0.25 mm capillary to become blocked by phosphoric acid that can enter the space underneath the working electrode. It also prevents pressure build-up in the cell.

The phosphoric acid doped PBI membrane and the cell body are stacked on top of the GDE. The membrane is protected by placing a slight overlap of PTFE foil between the edge of the GDE and the membrane.
Figure 2.1: Sketch of the HT-PEM DEMS cell design: (1) nozzle connected to gas inlet, (2) working electrode, (3) supporting PEEK sieve, (4) electric contact, (5) PBI membrane, (6) gas outlet and connection to MS, (7) borosilicate glass-filter, (8) counter electrode, (9) Luggin capillary, (10) hydrogen reference electrode in the same media, (11) copper heating plate, (12) glass-encased heating finger, (13) and (14) thermocouples, (15) thermal insulation.
The body of the cell (height *ca.* 70 mm, inner diameter 25 mm) contains concentrated phosphoric acid (H$_3$PO$_4$). On the underside it has an opening containing a removable borosilicate glass-filter (7), which allows the electrolytic contact of the solution with the membrane, while compressing the membrane and WE to reduce Ohmic and contact resistance. A Pt net counter electrode (CE) of big area (8) and a Luggin capillary (9) connecting a reference electrode (10) are suspended inside the cell body through conically tapered holes in the top of the cell. In addition, a small nozzle exists to facilitate the escape of evaporated water at high temperature.

The three cell parts of the set-up are stacked on top of a copper heating plate and a mount that can be held by a clamp. A flat PTFE gasket is used to seal the connection between cell bottom and cell body. All parts are vertically connected by four threaded bars (diameter 4 mm) and fixed with nuts at the top and bottom of each bar. The nuts were then tightened transversely.

The cell can be fed with diverse gaseous reactants as well as with liquid reactants, provided they can be vaporized at temperatures below roughly 180 °C. Gaseous reactants are heated up to 120 °C before entering the cell, in order to prevent abrupt temperature changes in the cell, while liquid fuel is evaporated using an electrically heated microstructured heater obtained from the Institute for Micro Process Engineering at Karlsruhe Institute of Technology (KIT) [137].

The body of the cell is electrically heated by two independent control loops due to the different heat capacity of the body and bottom of the cell. The bottom part of the cell is heated from underneath by a home-made heating copper plate (11). The body of the cell is heated with a home-made glass-encased heating finger inside the electrolyte (12). Both are regulated via one thermocouple each inside the built-in heating cartridges, and a second thermocouple is installed close to the heating cartridges in each heating device for safety shutoff.

The temperature inside the cell is measured by two additional thermocouples. One of them (13) is encased in a closed-off PEEK capillary and situated inside the chamber underneath the working electrode. The second thermocouple (14) is encased in a glass capillary and situated inside the electrolyte. In addition the electrochemical cell is fully thermally insulated (15) in order to avoid temperature irregularities.
Figure 2.2: Sketch of the peripheral equipment of the HT-DEMS set-up.

The cell design was loosely based on an existing flow cell for DEMS measurements on supported catalyst at ambient temperature \[^{[83]}\]. Originally, the conic shape of the reaction chamber in the bottom of the cell was designed to lead to a hole in its ground that would facilitate flanging it directly onto the entrance to the MS to use membrane connection at ambient temperature measurements as an alternative to the capillary connection. However, that concept was dropped as it became clear that the cell bottom, which was originally made of stainless steel, could not withstand corrosion under the given conditions, though several approaches had been tried to render the inside of the cell inert.

This led to the idea to make a new cell bottom from PEEK which had already proven an appropriate material for the cell body. The PEEK version of the cell body was modeled after the stainless steel version, but another solution had to be found to lead the incoming ethanol to the GDE as this had previously been accomplished with a 90° bent stainless steel capillary. This 90°
angle could not be realized with a PEEK capillary, and so the fixed nozzle leading up from a fuel inlet channel in the cell bottom was implemented.

Changing the material of the cell bottom to an electrical isolator also had the consequence of complicating the electrical connection between the working electrode and the outside of the cell from where it could be connected to the potentiostat. The gold net between the GDE and the PEEK sieve has proven suitable for collecting and conducting the electrical currents from the GDE. However, while a solution has been found for sealing the connection between cell body and bottom with home-made non-reusable flat gaskets that can accommodate a small band of gold net to lead outside the cell, the electrical connection of the working electrode remains one of the weaknesses of the set-up and a more durable solution has yet to be found.

It also became apparent that heating only from inside of the cell body was not effective enough to heat the cell up to temperatures close to 200 °C, because the way the cell is mounted means the temperature loss from the bottom of the cell to the holder underneath cannot easily be avoided and attempts to create a more effective thermal insulation failed. Thus in addition to the existing heating the copper heating plate was implemented directly underneath the cell. The heating of the cell turned out to be rather complex, because of a) the heat conduction properties and temperature limitations of the PEEK material that had to be considered and b) the different thermal capacity of the phosphoric acid filled container on top and the smaller bottom of the cell that nonetheless had to be heated up at a similar rate. All this results in a sluggish heat build-up in the cell, which takes around an hour to heat up from ambient temperature to a working temperature of 150 °C.

Another persisting issue of the set-up that requires a slow heat build-up is the polymer membrane. The PBI underneath the phosphoric acid can still increase its doping level at high temperatures and thus swell which may lead to stress on the material. As a result the membrane can break and phosphoric acid can leak into the reaction chamber and in the worst case block the capillary leading to the MS. The use of PTFE frames to protect the membrane from the edges of the GDE has been found to lessen this problem, but it can’t yet be completely prevented.
2.1.2 Chemicals and materials

In all the experiments a large area platinum net electrode was used as counter electrode (CE). In order to avoid contaminations it was cleaned in a mixture of concentrated H\textsubscript{2}SO\textsubscript{4} and 30\% H\textsubscript{2}O\textsubscript{2} (3:1) before each series of measurements. The reference electrode was a reversible hydrogen electrode (RHE) in the same medium connected via a Luggin capillary. The homemade RHE electrode consisted of a Pt net electrode inside a small glass bell with a ca. 1 mm diameter hole on the underside. The glass bell was filled with concentrated phosphoric acid, so that no gas bubbles remained inside, and then a bubble of hydrogen was formed at the Pt net by electrolysis. The RE was cleaned and renewed before each series of measurements. All potentials given are with respect to this reference electrode.

The polymer membrane was a PBI membrane fumapem AM from Fumatech. It was acid doped by heating in 85\% H\textsubscript{3}PO\textsubscript{4} in nitrogen atmosphere for 3 hours at 150 °C and slow cooling to room temperature. The acid doped level of 12 M H\textsubscript{3}PO\textsubscript{4}/ABPBI was determined by weighing of the membrane before and after acid doping.

The H\textsubscript{3}PO\textsubscript{4} used for membrane preparation as well as in the set-up was 85\% o-phosphoric acid p.a. from Roth. For use in the set-up, the H\textsubscript{3}PO\textsubscript{4} was heated up to ca. 150 °C and evacuated for several hours to remove water and avoid the formation of water gas bubbles in the set-up, especially inside the Luggins-capillary.

The ethanol solutions used were 10.9 M (500 g/L), 5 M and 1M ethanol absolute p.a. from Merck in ultrapure water (Purelab Ultra 0.055 µS/cm at 25 °C).

The potentiostat used was a Solartron SI 1287 for the measurements presented in Chapters 4 and 5 and a Gamry Reference 600 for the measurements in Chapters 3, 6, and 7.
2.1.3 Catalyst synthesis

The PtRh/C bimetallic catalysts were synthesized using a modified polyol method. The advantages of this procedure are its high simplicity and the ability to control the particle size of the metal nanoparticles which are formed on the carbon support by varying the pH.

The metal precursors used were $\text{H}_2\text{PtCl}_6$ and $\text{RhCl}_3\cdot x\text{H}_2\text{O}$ ($x = 0$-3) or water free $\text{RhCl}_3$ (all from Aldrich). While the $\text{RhCl}_3$ containing water of crystallization can be readily dissolved, the water free $\text{RhCl}_3$ can takes several hours at elevated temperature and vigorous stirring to dissolve in the EG/water mixture.

In the first step, the amount of metal precursor(s) necessary for the desired catalyst loading on the carbon support are weighed and dissolved in a mixture of ethylene glycol (EG) and milli-Q water with the volume ratio 1:1.

In the second step, the carbon support (carbon black particles Vulcan XC-72R, Cabot) is dispersed by sonication in more of the same mixture of EG and water, and then added to the metal precursor solution. Afterwards, EG is added to the reaction mixture in order to obtain a 2:1 volume ratio of EG to water.

In a third step the pH of the solution is adjusted to pH = 12 by slow addition of a solution of 0.5 M NaOHin EG/water (1:1) under vigorous stirring. The mixture is then stirred at ambient temperature for 1 h while argon is bubbled through the solution.

In the last step the mixture is heated up to 160 °C and boiled for 3 h under reflux. After that, the argon flow is stopped and the mixture is left to cool overnight in air. The catalyst is then filtered, washed with milli-Q water until neutral and dried overnight at 80 °C.

Typical batch size was 100 mg catalyst, using 20 mL of the 1:1 EG/water mixture for the metal solution and carbon particle dispersion each, and adding 20 mL EG to reach the 2:1 EG/water ratio. The batch size could be scaled up to 1 g, using a minimum of 70 mL of the solutions instead.
2.1.4 Electrode preparation

The working electrodes used were GDEs prepared by spray-coating Sigracet® GDL 10AA carbon paper gas diffusion layers (GDLs) from SGL Group with either commercial Pt black, commercial 10% Pt/C catalysts, both from Alfa Aesar, or the above prepared PtRh/C catalysts.

A catalyst ink was mixed by first adding water to the catalyst under stirring. Secondly, ethanol was added in the weight ratio ethanol/water ca. 2.5:1, because it improves the flow behavior of the catalyst ink. Ethanol cannot be used, however, with Pt black catalysts, because the risk of spontaneous combustion is too high. It is also not used in cases where a solely aqueous mixture already showed a suitable viscosity for spray-coating. The amount of solvent added to each catalyst ink depended on the catalyst. To reach the desired viscosity a weight ratio solvent/catalyst around 12:1 was in most cases sufficient (cf. Table 2.1).

Table 2.1: Catalysts used for GDE manufacture and their ink composition. The composition of the PtRh/C catalysts was determined via ICP.

<table>
<thead>
<tr>
<th>#</th>
<th>Catalyst type</th>
<th>PTFE emulsion wt%</th>
<th>Water wt%</th>
<th>Ethanol wt%</th>
<th>Catalyst wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Pt black</td>
<td>7.4</td>
<td>7.4</td>
<td>-</td>
<td>85.2</td>
</tr>
<tr>
<td>II</td>
<td>10%Pt/C</td>
<td>7.0</td>
<td>2.7</td>
<td>6.6</td>
<td>83.7</td>
</tr>
<tr>
<td>III</td>
<td>10%PtRh/C: 5.14% Pt, 4.95% Rh</td>
<td>7.0</td>
<td>2.5</td>
<td>6.7</td>
<td>83.8</td>
</tr>
<tr>
<td>IV</td>
<td>10%Pt/C</td>
<td>6.9</td>
<td>2.7</td>
<td>7.1</td>
<td>83.3</td>
</tr>
<tr>
<td>V</td>
<td>Pt black</td>
<td>6.8</td>
<td>10.5</td>
<td>-</td>
<td>82.7</td>
</tr>
<tr>
<td>VI</td>
<td>7.35% PtRh/C: 4.38% Pt, 2.97% Rh</td>
<td>6.8</td>
<td>11.4</td>
<td>-</td>
<td>81.7</td>
</tr>
</tbody>
</table>

To form a homogenous dispersion the ink was sonicated for 30 minutes in an ice bath \[^{138}\] ; then left to stir overnight at 200-250 rpm. After this PTFE (ca. 5 wt% referring to solid catalyst) from DuPont™ Teflon® emulsion TFE-3859 (containing ca. 60 wt% PTFE) was added as binder. The addition of the emulsion containing the binder was done drop by drop under sonication in an ice bath. The ink was then homogenized under sonication for at least 45 minutes. The finished ink was continuously stirred until spraying.

The GDL was heated on top of a heating plate to 110-120 °C during spraying, so that the catalyst layer could dry quickly and evenly without running or cracking. When necessary an infrared
lamp was used to provide additional heat from above. The gas used for spraying was 0.7-1 bar\textsubscript{g} argon with a Schütze spray pistol.

After spraying the GDEs were dried in an oven for 1 h at 130 °C, and laminated at the same temperature and a pressure of 1 kN/cm\textsuperscript{2}.
2.2 Electrochemical methods

2.2.1 Cyclic voltammetry

In a cyclic voltammetric (or cyclovoltammetric) measurement in a three electrode assembly (Figure 2.2) a dynamic potential is applied between the working electrode (WE) and the reference electrode (RE). The resulting current is measured between the WE and the counter electrode (CE). The applied dynamic potential signal is changed with a constant rate over time, the scan rate \( v = \frac{dE}{dt} \). Beginning at a starting potential the scan usually precedes in the direction of higher potentials until the upper vertex potential is reached. Here the direction of the scan is reversed and the potential is decreased until the lower vertex potential is reached, where the scan direction is reversed again and the potential increases until the starting potential is reached. This cycle can be repeated any number of times, for example to observe time sensitive changes in the resulting measurements.

Figure 2.3: Schematics of a CV set-up, WE – working electrode, CE – counter electrode, RE – reference electrode.
Figure 2.4A shows the applied potential over the time and illustrates the method of the measurement. Figure 2.4B shows a possible resulting current if a redox reaction occurs during the measurement. The cyclic voltammogram (CV Figure 2.4C) is the plot if the current over the potential.

In aqueous solutions the vertex potentials are limited by the electrolysis potentials of water at which gaseous oxygen or hydrogen are formed at the specific electrode. The shape of the CV is influenced by several factors. On the one hand, it is dependent on the surface composition and structure of the working electrode as well as the concentration and reaction of electrochemically active compounds in the electrolyte. On the other, experimental parameters like temperature, diffusion conditions as well as the scan rate of the CV measurement can significantly influence the processes at the electrode surface. Due to all these factors, and the complex reactions occurring at heterogeneous catalyst surfaces, interpretation of a CV is not trivial.
2.2.2 **Chronoamperometry**

There are limits to voltammetry as an experimental technique because of the constant change of experimental parameters due to the potential sweep. As rate constants and poison or adatom coverages are potential dependent, other techniques are needed for studies in the steady state.

During a chronoamperometric measurement a constant potential is applied to the working electrode in a three electrode set-up during a period of time while simultaneously the current response over time is recorded. The time dependent current curve can deliver information about reactions taking place at the electrode under steady state conditions.

In a simple chronoamperometric experiment, the potential at the working electrode is first held at a potential at which no reaction takes place, then the electrochemically active substance is added. Afterwards the potential is switched to the desired reaction potential. In the simplest case, that of a reversible diffusion controlled reaction, the educt is readily converted at the electrode. Under this condition the measured electrolysis current is diffusion controlled and can be described by the Cottrell equation (Equation 2.1).

\[
i = \frac{zFAC_0}{\sqrt{\pi \cdot t}} D c
\]

*Equation 2.1*

- \(i\) Electrolysis current
- \(z\) Number of electrons exchanged during the reaction
- \(F\) Faraday constant; \(9.6485 \cdot 10^4\) C/mol
- \(D\) Diffusion constant
- \(A_0\) Electrode surface
- \(t\) Time
- \(c\) Concentration of the electrochemically active substance in the electrolyte

If the reaction rate of the electrochemically active compound at the electrode is slower than its diffusion to the electrode surface, the Cottrell equation does not apply, because in this case the current is controlled by the reaction kinetic. Thus the current can only be described by a kinetic equation.

A redox couple reacting at the electrode of a half cell can be described as:
\[ S_{\text{red}} \rightleftharpoons S_{\text{ox}} + z \cdot e^- \]

Equation 2.2

where \( S_{\text{red}} \) is the reduced species, \( S_{\text{ox}} \) the oxidized species and \( z \) the number of electrons (\( e^- \)) exchanged during the reaction. If the oxidation and reduction reaction have the rate coefficients \( k_+ \) and \( k_- \) respectively, then the Arrhenius equation applies (Equation 2.3):

\[
k_+ = k_+^0 \cdot \exp\left(- \frac{\Delta G^\neq}{RT}\right)
\]

Equation 2.3

In this equation \( k_+^0 \) is the rate coefficient of the reaction under standard conditions, and \( \Delta G^\neq \) its free activation enthalpy (or activation energy). \( \Delta G^\neq \) is defined as the difference between the free enthalpy of the educts and the activated complex which is an energetically higher transition state occurring during the reactions.

In an electrochemical reaction the equilibrium of the reaction equation 2.2 can be shifted by applying a potential. If the potential at the start is \( \varphi_1 \) and is changed to \( \varphi_2 \), with \( \Delta \varphi \) the difference between the two potentials, this influences both the free enthalpy of the electrons in the electrode metal and the free enthalpy of the transition state.

The change of the free enthalpy on the oxidized site of Equation 2.4 is

\[
\Delta G_{\text{ox}}(\varphi_2) - \Delta G_{\text{ox}}(\varphi_1) = -z \cdot F \cdot \Delta \varphi
\]

Equation 2.4

with \( \Delta G_{\text{ox}}(\varphi_2) > \Delta G_{\text{ox}}(\varphi_1) \) if the potential is shifted in negative direction, so that \( \varphi_2 < \varphi_1 \) and \( \Delta \varphi < 0 \).

The change of the free enthalpy of the transition state has to be between this value and zero, which is achieved by introducing the charge transfer coefficient \( \alpha \).

\[
\Delta G^\neq(\varphi_2) - \Delta G^\neq(\varphi_1) = -\alpha \cdot z \cdot F \cdot \Delta \varphi
\]

Equation 2.5

with \( 0 < \alpha < 1 \).
Thus the change of the free activation enthalpy of the oxidation reaction is

\[ \Delta G^o_+ (\phi_2) - \Delta G^o_+ (\phi_1) = -\alpha \cdot z \cdot F \cdot \Delta \phi \]  \hspace{1cm} \text{Equation 2.6} \\

as illustrated in Figure 2.4, and the corresponding equation for the reduction reaction is

\[ \Delta G^-_-(\phi_2) - \Delta G^-_-(\phi_1) = (1 - \alpha) \cdot z \cdot F \cdot \Delta \phi \]  \hspace{1cm} \text{Equation 2.7} \\

![Figure 2.5: Free enthalpy along the reaction pathway with the applied potentials \( \phi_1 \) and \( \phi_2 \).](image)

If the kinetics of the reaction are of the first order, without any side or follow-up reactions, then the current flowing between the electrode and the electrolyte at a potential \( \phi \) is:

\[ i_+ (\phi_1) = z \cdot F \cdot c_{\text{red}} \cdot k_+ (\phi_1) \]  \hspace{1cm} \text{Equation 2.8} \\

for an anodic current and

\[ i_- (\phi_1) = -z \cdot F \cdot c_{\text{ox}} \cdot k_- (\phi_1) \]  \hspace{1cm} \text{Equation 2.9} \\

for a cathodic current.
In the latter $k'$ includes the concentration of the electrons in the electrode metal, which can be assumed to be constant due to the high electron mobility. $c_{\text{red}}$ and $c_{\text{ox}}$ are the concentrations of the reduced and oxidized species respectively.

With a shift to a potential $\phi_2$ the anodic and cathodic currents are:

$$i_+(\phi_2) = z \cdot F \cdot c_{\text{red}} \cdot k_+^0 \cdot \exp \left( - \frac{\Delta G^e_+ (\phi_1) - \alpha \cdot z \cdot F \cdot \Delta \phi}{R \cdot T} \right)$$  \hspace{1cm} \text{Equation 2.10}

or

$$i_-(\phi_2) = -z \cdot F \cdot c_{\text{ox}} \cdot k_-^0 \cdot \exp \left( \frac{\Delta G^e_- (\phi_1) + (1-\alpha) \cdot z \cdot F \cdot \Delta \phi}{R \cdot T} \right)$$  \hspace{1cm} \text{Equation 2.11}

If $\phi_1$ is defined as zero in relation to the reference electrode, then $\Delta \phi$ is the potential $\phi$ as measured against this reference electrode. Thus, with $i_\pm(\phi_1) = i_\pm^0$, the currents are:

$$i_+ (\phi) = i_+^0 \cdot \exp \left( \frac{\alpha \cdot z \cdot F \cdot \phi}{R \cdot T} \right)$$  \hspace{1cm} \text{Equation 2.12}

and

$$i_- (\phi) = i_-^0 \cdot \exp \left( \frac{(1-\alpha) \cdot z \cdot F \cdot \phi}{R \cdot T} \right)$$  \hspace{1cm} \text{Equation 2.13}
The overlap of the two current densities for the anodic and cathodic reaction leads to the Butler-Volmer equation which describes the relationship between the current and the electrode potential:

\[
i_\pm(\varphi) = i_+ (\varphi) + i_- (\varphi) = i_0 \cdot \left( \exp\left( \frac{\alpha \cdot z \cdot F \cdot \varphi}{R \cdot T} \right) - \exp\left( -\frac{(1 - \alpha) \cdot z \cdot F \cdot \varphi}{R \cdot T} \right) \right)
\]

Equation 2.14

As described in the Butler-Volmer equation the current \(i\) measured between the working electrode and counter electrode is the sum of both the anodic and the cathodic currents. At an applied potential which is sufficiently far from the equilibrium potential of the redox reaction, one of the two partial reactions prevails and the other becomes negligible.

As can be gained from the equations 2.10-2.14 the logarithm of the measured current is proportional to the applied potential. Commonly \(\ln |i|\) is plotted against \(\varphi\) in a so called Tafel plot. With \(\ln x = 2.3 \log x\) the slope \(m\) of this plot is:

\[
m = \frac{\alpha \cdot z \cdot F}{2.3 \cdot R \cdot T}
\]

Equation 2.15

at the anode, and

\[
m = \frac{(1 - \alpha) \cdot z \cdot F}{2.3 \cdot R \cdot T}
\]

Equation 2.16

at the cathode.

The apparent activation energy \(E_A\) of an electrochemical reaction (for a set potential) can be gained from the temperature dependence of the Arrhenius equation (2.3), with \(E_A\) corresponding to the free activation enthalpy \(\Delta G^\pm\) in the equation. The term \(E_A\) is used because the apparent activation energy is an empirical value, and cannot be equated with the free enthalpy of a certain transition state in the case of more complex electrochemical reactions.

\(E_A\) can be derived by a chronoamperometric measurement of the asymptotic limiting current of a reaction at different temperatures. The asymptotic limiting current is a constant current which is reached for \(t \to \infty\). In most cases it can be assumed that the limiting current is reached 15 minutes after the potential jump.

The method presumes that for \(t \to \infty\) an equilibrium is reached in which \(i \propto k\).
The logarithm of the current $i$ plotted against $T^{-1}$ (Arrhenius plot) shows a linear correlation with a negative slope. The slope multiplied with the universal gas constant $R$ gives the apparent activation energy $E_A$.

The Arrhenius plot is based on the logarithmic form of the Arrhenius equation, in which $\ln k$ and $\ln i$ respectively are inversely proportional to $T$ with the factor (or slope) $E_A/R$.

$$\ln k = \ln i = \ln A - \frac{E_A}{R} \cdot \frac{1}{T}$$

**Equation 2.17**

*K* Reaction rate coefficient  
*A* Pre-exponential factor  
$E_A$ Activation energy  
*R* Universal gas constant  
*T* Temperature in K

As with the potential dependency of the current as described above, is $i \propto k$ only strictly valid for electrochemical reactions without follow-up, side or reverse reactions.
2.3 Electrochemically active area

During a stripping experiment an electrochemically active compound is adsorbed on the working electrode which is held at a constant potential. During this time an adsorption current can be measured if the adsorption process on the electrode metal involves an electron exchange.

In a second step, the excess compound is removed from the working electrode, usually by flushing the cell with fresh electrolyte, and only a layer of adsorbate on the working electrode remains. Afterwards the potential, which has up to now been held constant, is changed in such a way that the adsorbate on the surface is desorbed, undergoing an electrochemical reaction. The potential can be changed either gradually by running a CV or suddenly by jumping to another potential.

Depending on the chosen compound, working electrode, and electrolyte matrix, a stripping experiment can yield information on the nature and amount of the adsorbate as well as on the physical and electrochemical properties of the working electrode.

The determination of the real or electrochemically active surface of an electrode is generally conducted by measuring the adsorption of either hydrogen or carbon monoxide on the active sites of the Pt catalyst. The amount of adsorbed hydrogen can be determined from the oxidative current occurring during its desorption in an anodic potential scan. The amount of adsorbed carbon monoxide can be determined from the oxidative current during its oxidation to carbon dioxide in an anodic potential scan.

2.3.1 Via hydrogen adsorption

The determination of the electrochemically active surface via hydrogen adsorption can be done according to Biegler et al. \cite{139}. The oxidative current occurring during hydrogen desorption is measured during an anodic potential scan. The area under the curve in the hydrogen desorption area is directly proportional to the amount of hydrogen adsorbed on the Pt surface and the surface size. Since the experimental conditions can strongly influence the measured current, to gain results comparable to those given in literature, the experiment has to be carried out in 0.5 M (or 1 N) H₂SO₄ at ambient temperature. It should also be taken into account that the original
experiments have been done with analogous potentiostats. When measuring with a digital potentiostat, the area under the curve can be influenced by the size of the potential steps used during the scan as well as the time between the potential step and the measuring of the current.

Corrected for the double layer capacitance, the exchanged charge can be determined. The charge exchanged per area for one hydrogen atom per Pt atom is assumed to be 210 µC/cm². This conventional standard for polycrystalline Pt is derived from the contributions of the three single crystal surfaces given in Table 2.2.

Table 2.2.2: Charge exchange per area on monocrystalline and polycrystalline Pt surfaces.

<table>
<thead>
<tr>
<th>Pt</th>
<th>Charge exchange per area (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>241</td>
</tr>
<tr>
<td>(100)</td>
<td>209</td>
</tr>
<tr>
<td>(110)</td>
<td>200</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td>210</td>
</tr>
</tbody>
</table>

2.3.2 Via CO adsorption

As an alternative to the reductive adsorption and oxidative desorption of hydrogen other reversible adsorption reactions can be used for the determination of the electrochemically active surface area of an electrode. The choice of adsorbate depends on the electrode material and electrolyte in question.

Another appropriate method for platinum is the adsorption and oxidation of carbon monoxide. For this experiment CO gas is bubbled through the electrolyte until the electrolyte is saturated. The standard electrolyte is 0.5 M H₂SO₄, but due to the higher oxidation current and the strong adsorption of the CO, the method is much less sensitive to the potentiostat and the electrolyte used. The working electrode is held at a potential close to 0 V, but above the onset of hydrogen adsorption. The resulting surface coverage of the polycrystalline Pt surface upon saturation with CO has been determined at ambient temperature and in dilute H₂SO₄. On Pt (100) a p(3√2×√2)R45° structure with a coverage of ⅔ monolayer (ML) can be formed. On Pt (111)
the highest possible coverage is a (2×2) 3CO structure with a coverage of 0.75 monolayers (ML) which is only formed at high CO partial pressure while at low partial pressure an equilibrium coverage is reached at 0.68 ML \cite{142} or 0.67 ML \cite{143}. On polycrystalline Pt Schmidt et al. measured a saturation coverage of 0.68 ML \cite{144}. However, Kohlmayr and Stonehart \cite{145} determined equilibrium coverages on polycrystalline Pt in concentrated H$_3$PO$_4$ at temperatures between 105 and 148 °C and found a significantly lower CO coverage of 0.58 ML at low CO partial pressure.

In the next step the excess CO is removed from the electrolyte by flushing it with an inert gas like argon or nitrogen or exchanging the electrolyte in case of a flow cell. Afterwards a CV is performed starting at the set potential and going in anodic direction. At a potential around 0.6 V vs. RHE the adsorbed CO starts to be oxidized to CO$_2$ which is desorbed from the electrode surface. The reaction is fast and complete and yields two electrons for every adsorbed CO molecule.

After the stripping cycle two more cycles are recorded which should be identical to each other and to the background CV for the electrode in the electrolyte. The second cycle is used as baseline for the integration of the CO oxidation peak. By using the background CV as baseline, the measurement of the oxidation current is corrected for the double layer current and the oxidation current of the platinum oxide formation setting in around 0.7 V.

The surface is then calculated by dividing the graphically derived charge $Q_{CO}$ by the product of surface coverage, number of exchanged electrons, and charge exchange per area for polycrystalline platinum.

$$A_{\text{real,CO}} = \frac{Q_{CO}}{0.68 \cdot 2 \cdot 210 \mu C / cm^2}$$

Equation 2.18
Figure 2.6: CO stripping CV and baseline in 0.5 M H$_2$SO$_4$ and difference of both curves (scan rate 10 mV/s at 20 °C).
3 CO oxidation

3.1 CO stripping

The electrooxidation of adsorbed CO to CO$_2$ during an anodic potential sweep, also known as CO stripping, can be used to determine the electrochemically active surface area (ECSA) of a catalyst as well as to correlate the ion currents measured in the MS to a known amount of produced CO$_2$ [55]. Furthermore, it is well known that CO acts as a catalyst poison in low temperature PEMFCs [146]. In contrast, CO adsorption at elevated temperature is reduced [145,147,148], which is a major advantage of HT-PEMFC over LT-PEMFC.

3.1.1 Determination of electrochemically active surface area (ECSA)

CV measurements of the oxidation of adsorbed CO on 10% Pt/C electrocatalyst have been carried out at 150 °C (cf. Figure 3.1).

To conduct a CO stripping experiment the potential of the electrode was held at 170 mV while pure CO was injected into the cell for 5 minutes. After that, still keeping the potential constant, the CO gas injection was again substituted by humidified N$_2$ and the cell was purged for 13 minutes to remove all CO gas. When the cell was flushed with N$_2$ the potential was swept at 10 mV/s in order to oxidize the layer of CO adsorbed on the Pt electrocatalyst surface.

Parallel to the electrochemical CV, MS signals were recorded over time, and the data combined to give mass spectrometric cyclic voltammograms (MSCVs). In Figure 3.1b and 3.1c the MSCVs for mass to charge ratios $m/z = 44$ and 22 (corresponding to CO$_2$) during the CO oxidation are presented. In the first cycle significant amounts of CO$_2$ are detected which are formed by oxidation of CO$_{ads}$.

A small ion current signal corresponding to CO$_2$ is again observed in the 2$^{nd}$ cycle. However, signals of similar amplitude are also observed during CV measurements in nitrogen atmosphere before CO injection (cf. Chapter 4), thus these signals are probably caused by CO$_2$ formed during
degradation of the carbon support. The 2\textsuperscript{nd} cycles have been taken into account as background for the determination of the area under the Faradaic current curve as well as the two ion currents.

3.1: CVs (scan rate 10 mV/s, 1st and 2nd cycle) (a) and MSCVs for m/z = 44 (b) and m/z = 22 (c) during oxidation of adsorbed CO on 10 \% Pt/C (1.42 mgPt/cm\textsuperscript{2}) at 150 °C.

Regarding the potential of the CO oxidation current peak, previous measurements on polycrystalline Pt electrodes have shown a significant shift of CO oxidation peaks to lower potentials when increasing the temperature to 70 °C. An onset for CO oxidation of 0.2 V and 0 V have been reported in aqueous sulfuric acid and potassium hydroxide solution respectively \cite{149}.
In the present measurements however, the CO oxidation peak in concentrated phosphoric acid has an onset of 0.5 V and a maximum at 0.7 V. These results are in agreement with those reported by Kohlmayr et al. [145] on a smooth Pt electrode in 96 % phosphoric acid at 135 °C. However the thermal activation of the CO oxidations in concentrated phosphoric acid is not as strong as in the aqueous solutions, which might be due to the lower water concentration at the electrode.

![Graph showing the Faradaic current integration](image)

3.2: Example for the integration of the Faradaic current in the forward (a) and backward (b) scan of the CV depicted in Figure 3.1.1 (a).

The area under the CO oxidation peak of the CV was determined by subtracting the second cycle from the first in the potential limits of 0.46 and 0.9 V in the anodic scan, and 0.9 and 0.64 V in the cathodic scan (cf. Figure 3.2). The calculation of the Faradic charge from Figure 3.2 is shown in Table 3.1.
Table 3.1: Example for the calculation of the Faradaic charge $Q_F$ from the areas determined from Figure 3.2.

<table>
<thead>
<tr>
<th></th>
<th>Area CV</th>
<th>Area CV</th>
<th>Area CV</th>
<th>$Q_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A^*V$</td>
<td>$A^*V$</td>
<td>$A^*V$</td>
<td>$C$</td>
</tr>
<tr>
<td>Backward scan</td>
<td></td>
<td></td>
<td></td>
<td>/0.01 V/s</td>
</tr>
<tr>
<td>Forward scan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurement 1</td>
<td>7.54·10^{-3}</td>
<td>4.37·10^{-3}</td>
<td>5.13·10^{-3}</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Considering the area of the peak and the scan rate used (10 mVs), a charge of 510 mC corresponds to the oxidation of the adsorption layer of CO. The electrochemically active surface area $A_{\text{real,CO}}$ of the electrode can be calculated according to Equation 3.1 \[57\].

$$A_{\text{real,CO}} = \frac{Q_{\text{CO}}}{Q_{\text{th,CO}}} \cdot 0.68$$

Equation 3.1

Using the conventional theoretical charge $Q_{\text{th,CO}}$ of 420 µC per cm² electrochemically active surface area \[150\], a saturation coverage of 68% \[144\], dividing by the geometric electrode area of 2.84 cm² and taking into account the Pt loading of the electrode of 1.42 mgPt/cm² it is possible to determine an active surface area for the electrode.

Table 3.2: Calculation of the ECSA per geometric electrode area $A_{\text{geo}}$ and per Pt mass $m_{\text{Pt}}$ for three CO stripping measurements on the same electrode.

<table>
<thead>
<tr>
<th></th>
<th>$Q_F$</th>
<th>ECSA</th>
<th>ECSA per $A_{\text{geo}}$</th>
<th>ECSA per $m_{\text{Pt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µC</td>
<td>cm²</td>
<td>m²/cm²</td>
<td>m²/g Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>/420 µC/cm²</td>
<td>*0.0001</td>
<td>/2.84 cm²</td>
</tr>
<tr>
<td>Measurement 1</td>
<td>5.13·10^{-2}</td>
<td>1.80·10^{-3}</td>
<td>6.32·10^{-2}</td>
<td>44.52</td>
</tr>
<tr>
<td>Measurement 2</td>
<td>3.70·10^{-2}</td>
<td>1.30·10^{-3}</td>
<td>4.57·10^{-2}</td>
<td>32.16</td>
</tr>
<tr>
<td>Measurement 3</td>
<td>5.20·10^{-2}</td>
<td>1.82·10^{-3}</td>
<td>6.41·10^{-2}</td>
<td>45.15</td>
</tr>
</tbody>
</table>

These values are slightly lower than the $>50$ m²/gPt expected for a Pt/C catalyst \[151\], which could be caused by an excess of phosphoric acid on the catalyst layer or by a lower CO coverage due to the high temperature. A significant difference can be observed between the first two measurements, while a third CO stripping experiment performed on the same electrode on the next day shows a similar ECSA as the first measurement, confirming an ECSA of ca. 45 m²/gPt. It is possible that the ECSA of the second measurement is low because no saturation of the CO coverage on the catalyst surface was reached.
However, it is important to note that under the experimental conditions the method only allows an estimation of the active surface area, since the saturation coverage can be expected to be lower at high temperature \(^9\) and double layer charging effects are neglected.

### 3.1.2 Determination of the calibration constants for the MS ion current signals

In addition, CO oxidation measurements can be used to quantify the amount of CO\(_2\) detected as MS signals \(m/z = 22\) and \(m/z = 44\), and correlate this amount with the CO\(_2\) formed in the oxidation of CO\(_{ads}\) according to equation 3.2 \(^{57}\).

\[
K^*_{CO_2} = 2 \cdot \frac{Q_{MS}}{Q_F} \tag{Equation 3.2}
\]

To this end, the mass spectrometric ion currents are plotted over time and integrated to gain the ion charge detected during each of the three cycles (cf. Figure 3.3).

The resulting calibration constants \(K^*_{CO_2}\) are \((1.14 \pm 0.07) \cdot 10^{-7}\) for \(m/z = 44\) and \((1.7 \pm 0.2) \cdot 10^{-9}\) for the \(m/z = 22\) signal. The evaluation of \(K^*_{CO_2}\) is crucial in order to calibrate the parameters measured. The constant correlates the ion currents measured by the MS with the Faradaic current measured at the working electrode during CO\(_2\) formation. It depends on the chemical compound and the intensity of its \(m/z\) signal in question, on the set-up and experimental parameters of the mass spectrometer \(^{55}\).

With these results it is possible to evaluate the CO\(_2\) charge efficiency (CCE) using equation 3.3 \(^{57}\).

\[
\text{CCE} = \frac{n_i \cdot Q_{MS,i}}{K^*_{i} \cdot Q_F} \tag{Equation 3.3}
\]

The number of transferred electrons \(n_i\) for the complete oxidation of ethanol to one molecule of CO\(_2\) is 6. \(Q_{MS,i}\) is the mass spectrometric charge determined as the area under the \(m/z = 22\) ion current curve over time, \(K^*_{i}\), or in this case \(K^*_{CO_2}\) is the constant for \(m/z = 22\) determined via the CO oxidation above, and \(Q_F\) is the Faradaic charge of the ethanol oxidation.
The standard deviation for the calibration constants is around 5% for \( m/z = 44 \) and around 6% for \( m/z = 22 \). This should be kept in mind as any CO\(_2\) efficiency calculated will have at least that error that is probably due mainly to the noise of the mass spectrometric measurements. In fact since a similar error can be assumed for any ratio of charges calculated from Faradaic currents and ion currents under similar conditions, the error of the CO\(_2\) efficiency can be assumed to be between 10 and 15%.

There might also be an underestimation of the ECSA because the Faradaic carbon support corrosion current that is subtracted from the CO oxidation current with the 2\(^{\text{nd}}\) cycle is probably suppressed in the presence of CO. However this current is not easily quantifiable and thus removable from the rest of the background.

Table 3.3: Calculation of the ECSA mass spectrometric calibration constants \( K_{CO_2} \) for \( m/z = 22 \) and 44 for three CO stripping measurements on the same electrode.

<table>
<thead>
<tr>
<th>Q(_F)</th>
<th>Q(_{MS\ 22})</th>
<th>Q(_{MS\ 44})</th>
<th>( K_{CO_2,22}^e )</th>
<th>( K_{CO_2,44}^e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 1 – Cycle 2</td>
<td>Cycle 1 – Cycle 2</td>
<td>( m/z = 22 )</td>
<td>( m/z = 44 )</td>
<td></td>
</tr>
<tr>
<td>Measurement 1</td>
<td>0.51</td>
<td>( 4.36 \cdot 10^{-10} )</td>
<td>( 2.97 \cdot 10^{-8} )</td>
<td>( 1.70 \cdot 10^{-9} )</td>
</tr>
<tr>
<td>Measurement 2</td>
<td>0.37</td>
<td>( 2.94 \cdot 10^{-10} )</td>
<td>( 1.98 \cdot 10^{-8} )</td>
<td>( 1.59 \cdot 10^{-9} )</td>
</tr>
<tr>
<td>Measurement 3</td>
<td>0.52</td>
<td>( 4.82 \cdot 10^{-10} )</td>
<td>( 3.11 \cdot 10^{-8} )</td>
<td>( 1.85 \cdot 10^{-9} )</td>
</tr>
</tbody>
</table>
Figure 3.3: Ion currents of m/z = 22 (a) and 44 (b) over time with baseline and limits used for integration.
3.2 CO oxidation

3.2.1 On Pt/C

Figures 3.4 and 3.5 show the CO stripping CVs and MSCVs on a Pt/C catalyst at 150 and 130 °C respectively. The upper vertex potential is 1.0 V and no complete oxidation of CO is achieved in the forward scan, leading to a Faradaic oxidation current that can be observed in the backward scan as well as a trailing mass spectrometric signal. In addition, at both temperatures a formation of CO$_2$ is detected during the backwards scan, in the 1$^{st}$ cycle underneath the CO$_2$ formation during CO oxidation as well as in the subsequent two cycles. This effect is increased at higher temperature.

At 130 °C there are small maxima in the ion currents during the 2$^{nd}$ and 3$^{rd}$ scans with a maximum around 0.64 V. At 150 °C a similar smaller oxidation wave exists around 0.55 V that can be seen in the magnification (cf. Figure 3.6). These maxima might not be indicative of CO remaining in the system from the CO stripping experiment, but of CO$_{ad}$ species that are formed during carbon corrosion of the support. A small CO$_2$ formation around 0.6 V is consistent with the measurements done on Pt black in nitrogen atmosphere (cf. Chapter 4).

Furthermore, the lower temperature leads to a shift of the onset and maximum to a higher potential. At 150 °C (cf. Figure 3.4) the onset of CO oxidation is around 0.25 V and the maximum around 0.60 V. At 130 °C (cf. Figure 3.5) the onset is around 0.47 V and the maximum around 0.67 V. In both measurements there is no significant delay between the maximum in the Faradaic current and the maximum in the mass spectrometric currents. The maximum in the ion currents that occur during the backward scan at 150 °C culminate around 0.90 V in the 1$^{st}$ cycle, due to overlapping with the trailing signal from the CO oxidation, and at 0.88 V in the subsequent cycles. At 130 °C the maximum can only be determined in the 2$^{nd}$ and 3$^{rd}$ cycles at 0.87 V while the 1$^{st}$ cycle shows only a slight shoulder instead of an ion current maximum in the backward scan.
Figure 3.4: CV (a) and MSCV for \( m/z = 44 \) (b) and 22 (c) during CO stripping on 10% Pt/C 1.25 mg/cm\(^2\), scan rate 10 mV/s, at 150 °C.
Figure 3.5: CV (a) and MSCV for $m/z = 44$ (b) and 22 (c) during CO stripping on 10% Pt/C 1.25 mg/cm², scan rate 10 mV/s, at 130 °C.
CO₂ evolution during the backwards scan is attributed to carbon corrosion at high potentials, though it is uncertain why the CO₂ formation only happens during the backwards scan. The CO₂ formation being result of carbon corrosion is further supported by the observation that the effect is less severe but also observable at lower temperature.

### 3.2.2 On PtRh/C

A CO stripping measurement on PtRh/C catalyst is reproduced in Figure 3.7. In that measurement a higher upper vertex potential of 1.2 V leads to complete CO oxidation during the forward scan of the 1st cycle. Again CO₂ formation is detected in the mass spectrometric measurements during the backward scan.

The Faradaic oxidation wave during CO stripping has its onset at 0.60 V and its maximum at 0.73 V. The MSCVs show a slight delay in these measurements with an onset at 0.62 V and a maximum at 0.77 V, corresponding to a delay of 2 to 4 seconds between CO₂ formation and detection. The ion current in the backward scan has a peak at 1.07 V.
Figure 3.7: CV (a) and MSCV for $m/z = 44$ (b) and 22 (c) during CO stripping on 10% PtRh/C 1.05 mg/cm$^2$, scan rate 10 mV/s, at 150 °C, CO stripping.
Figure 3.8: CV (a) and MSCV for \( m/z = 44 \) (b) and 22 (c) during CO bulk oxidation on 10% PtRh/C 1.05 mg/cm², scan rate 10 mV/s, at 150 °C.
A measurement under CO atmosphere (cf. Figure 3.8) shows a small shoulder around 0.75 V when the preadsorbed CO is oxidized. It coincides with the onset of oxide formation on the catalyst surface, starting at a slightly higher potential than the more distinct shape of the CO oxidation wave measured during CO stripping. This is likely due to catalyst poisoning by the bulk CO present.

Going to higher potentials there is an increase in the oxidation current as the reaction rate of the CO oxidation form the bulk increases with rising potential. After inversion of the potential scan the Faradaic current caused by CO oxidation decreases again, but an oxidative current compared to the background measured in nitrogen atmosphere can be observed down to a potential around 0.4 V. The ion currents indicating the CO$_2$ formation show a shoulder corresponding to the oxidation of preadsorbed CO and then an increase that lasts into the backward scan with a peak around 0.9 V at an upper vertex potential of 1.0 V.

Figures 3.9 and 3.10 show two CV measurements in nitrogen atmosphere on the same catalyst with upper vertex potentials of 0.9 and 1.0 V respectively. In both cases CO$_2$ formation can be observed in the forward as well as in the backward scan. The maxima in the two measurements differ slightly with 0.70 V in the forwards scan and 0.80 V in the backwards scan for the measurement up to 0.9 V (Figure 3.9), and 0.73 V in the forward scan and 0.89 in the backward scan for the measurement up to 1.0 V (Figure 3.10). The first CO$_2$ formation might be connected to residues in the material of the gas diffusion electrode as it can be observed to decrease during cycling. In contrast, the CO$_2$ formation during the backwards scan seems to increase slightly with time and is influenced by the choice of upper vertex potential.
Figure 3.9: CV (a) and MSCV for $m/z = 44$ (b) and 22 (c) under N$_2$ atmosphere on 10\% PtRh/C 1.05 mg/cm$^2$, scan rate 10 mV/s, at 150 °C, before CO measurements (cf. Figures 3.7 and 3.8).
Figure 3.10: CV (a) and MSCV for \( m/z = 44 \) (b) and 22 (c) under \( \text{N}_2 \) atmosphere on 10% PtRh/C 1.05 mg/cm², scan rate 10 mV/s, at 150 °C, after CO measurements (cf. Figures 3.7 and 3.8).

A further CO stripping measurement on another PtRh/C electrode is reproduced in Figure 3.11. It was performed after changes in the set-up and the mass spectrometric measurement did not reach
the same quality as previously. Nonetheless, the formation of CO₂ could be detected again during backwards scans in both CO oxidation and nitrogen atmosphere measurements (cf. Figure 3.12).

In these measurements the ion current maximum during the backward scan is smaller in the 1ˢᵗ cycle of the CO stripping experiment than in the subsequent cycles (cf. Figure 3.11). The reaction or reactions responsible for the CO₂ formation might be hindered in this case by residual adsorbed CO.

The ion current spikes that can be seen in the backward scan of the CO stripping measurement could be caused by the very dry conditions at the high temperature. This might lead to an uneven supply of water and sudden formation of CO₂ when water is available at the catalyst surface. However, considering the very low values of the ion current they could also be an artefact caused by a blockage in the capillary leading to the MS.

Nonetheless, the CO₂ detected during the backward scan is consistently present and visible in background measurements and CO stripping measurements. It can likely be attributed to carbon corrosion. Several CO stripping and background measurements from the series of measurements on catalyst VI were analysed to calculate the amount of carbon oxidized during each cycle (cf. Figure 3.13). The calculation has been done with the mean of the calibration constants for m/z = 44 of the three CO stripping measurements. The mean has a standard deviation of 7 %, resulting in a total standard deviation of at least 14 % for the resulting values for carbon degradation.

The resulting values are spread over a wide range from ca. 17 to 38 µg carbon per cycle. The only obvious trend is that the 2ⁿᵈ cycle during CO stripping measurements shows consistently less carbon corrosion than the 3ⁿᵈ. This could be due to a poisoning effect of some remaining CO during the 2ⁿᵈ cycle, as Pt catalysts have been found to promote carbon corrosion. There is no obvious connection between the extent of carbon corrosion and the order in which the measurements were performed.
Figure 3.11: CV (a) and MCV for $m/z = 44$ (b) and 22 (c) during CO stripping on 7% PtRh/C (catalyst VI) 0.92 mg/cm$^2$, scan rate 5 mV/s, at 150 °C.
Figure 3.12: CV (a) and MSCV for m/z = 44 (b) and 22 (c) in nitrogen atmosphere before CO measurements on 7% PtRh/C (catalyst VI) 0.92 mg/cm², scan rate 5 mV/s, at 150 °C.
Figure 3.13: Carbon degradation during different measurements on 7% PtRh/C 0.92 mg/cm², scan rate 5 mV/s, at 150 °C.
3.3 Determination of delay time for CO\textsubscript{2}

When conducting DEMS measurements there is a delay time in between the electrochemical formation of products and their detection in the MS. This delay time depends on the distance between the working electrode and the ionization chamber of the MS as well as the pressure gradient between cell and MS. Another factor is dead volume in the cell.

In DEMS using a PTFE membrane this delay time can be expected to be around 1 s. Using a capillary as a connection to the MS however results in a significantly longer delay time.

Apart from the fact that the working electrode in the set-up is a gas diffusion electrode, which already causes some delay and mixing, there is a significant dead space underneath the working electrode which can be seen in the schematic diagram of the cell (cf. Figure 2.1). Thus, the connection to the MS is not as fast and as direct as in the case of a usual DEMS set-up which uses an electrode layer on a PTFE membrane directly on top of the vacuum chamber of the MS.

The cell design does indeed cause an increased response time compared to regular DEMS set-ups. In comparison to the volume of the space underneath the working electrode, mentioned above, the volume of the rest of the capillary outlet is negligible.

The response time cannot accurately be gained from the CV measurements, because the signal is somewhat broadened in addition to the delay. Often the delay between the onset of the Faradaic current and the ionic current can be seen to be smaller than the delay between the maxima of an oxidation wave. In the case of most CVs the delay time is around 1 s which is close to the time resolution of most of the MS measurements conducted. For this reason, unless explicitly stated, no corrections regarding the delay time have been made in the measurements presented.

An attempt was made to determine the delay time of the set-up for CO\textsubscript{2} (m/z = 44) by applying a potential jump under a CO atmosphere (cf. Figure 3.14). There is a significant drag in the mass spectrometric signal, but the onset of the increase and decline in the ion current after changing the electrode potential are comparatively fast with a delay time of \textit{ca.} 10 s. This would agree with the maxima in CO\textsubscript{2} formation observed around 0.1 V into the backward scan at a scan rate of 10 mV/s, although it cannot explain the apparently shorter delay time observed during CO stripping.
Figure 3.14: Faradaic current and ion current for m/z = 44, corresponding to formation of CO$_2$ during potential jump from 0.1 V to 0.65 V for 120 s and back to 0.1 V, on 10% PtRh/C 1.05 mg/cm$^2$, under CO atmosphere at 150 °C.
3.4 Discussion and Conclusions

CO stripping measurements were carried out to determine the calibration constants for the mass spectrometer. The corresponding calculations were shown for one series of measurements. The standard deviation of CO\textsubscript{2} charge efficiencies calculated from integration of the Faradaic current and ion current for the mass to charge ratios corresponding to CO\textsubscript{2} can be assumed to be at least 10\%, more likely around 15\%. The inaccuracy is probably due to dead volume in the experimental set-up and the connection of the cell to the MS via heated capillary which is less direct and more prone to being blocked than a connection via a porous membrane.

This also leads to a delay time between CO\textsubscript{2} formation and the detection in the MS. The delay time has been quantified by comparing the occurrence of the peaks in the oxidation wave and CO\textsubscript{2} detection during CO stripping measurements as well as CO\textsubscript{2} formation during a potential jump under CO atmosphere. The CO\textsubscript{2} formed by carbon corrosion and during the potential jump as well as the CO\textsubscript{2} produced in CO bulk oxidation is detected with a delay of around 10 s. There is a significantly smaller shift between the onset and peak of the oxidation wave during CO stripping and its mass spectrometric detection however.

CO\textsubscript{2} formed most likely by carbon corrosion in the GDE can be detected in measurements in nitrogen atmosphere as well as during CO stripping. The effect has been quantified for one GDE where the carbon oxidized to CO\textsubscript{2} amounts to \textit{ca.} 17 to 38 µg carbon per CV cycle, with no apparent correlation to the succession of measurements.
4 The effect of temperature on the ethanol oxidation reaction on Pt black

4.1 CV and MSCV measurements catalysts in nitrogen atmosphere on Pt black electro-catalyst in the temperature range of 120 to 180 °C.

Early measurements in the HT-DEMS set-up were conducted on gas diffusion working electrodes sprayed with Pt black, with PTFE as binder. Pt black was chosen as a starting point because it was assumed that due to its lack of carbon support, the measurements would be less influenced by catalyst degradation compared to carbon supported catalysts \([21,23]\).

To establish a background, the set-up was flooded with nitrogen and CV measurements were conducted starting in the anodic direction at 0.5 V with an upper vertex potential of 1.1 V and a lower vertex potential of -0.1 V. Three cycles each were run at seven temperatures in the range of 120 to 180 °C starting at the lowest temperature and going up in 10 °C steps (cf. Figure 4.1).

It is apparent from the decreasing currents in the hydrogen desorption region (-0.1 to 0.2 V) and the oxide desorption region (1.0 to 0.6 V) that the CVs are significantly modified as the temperature is increased, indication a loss of active surface area. This can be due to catalyst degradation, dissolution, reprecipitation and agglomeration \([152]\) as well as to poisoning of the active surface by phosphate. Such poisoning effects of phosphate anion adsorption are known to exist for the oxygen reduction reaction (ORR) on Pt \([153,154]\).

In addition to adsorption of phosphate, that of biphosphate and other condensation products of phosphoric acid is possible. The condensation reaction of phosphoric acid is promoted by the accelerated loss of water especially at temperatures above 140 °C. A factor that should be kept in mind is also the low water content in the hot and concentrated phosphoric acid, which would also be expected to contribute to the lack of expected Pt features caused by water desorption or adsorption and electrolysis of water. At a potential of approximately 0.85 V the formation of surface oxide on Pt is evidenced. In the cathodic scan a peak is noted around 0.8 V corresponding to oxide desorption from the Pt surfaces.
Figure 4.1: CVs in nitrogen atmosphere on Pt black in the temperature range from 120 to 180 °C (scan rate 10 mV/s, 3rd cycle).

In the potential window between 0.25 V and 0.8 V in the anodic scan as well as between 0.6 V and 0.25 V in the cathodic scan a redox couple can be observed with the oxidation and reduction current maxima around 0.5 V. While phosphate is known to undergo adsorption and deprotonation on Pt(111) planes in this potential window \[155-158\], the shape of the CV could as well be related to adsorption processes on the carbon surface.

It is unexpected that there seem to be characteristics for carbon surface oxides on the Pt black electrode, since no carbon support or microporous layer are present. This might be caused by processes on the surface of the GDL material itself. To validate this assumption a CV has been recorded on a GDL without catalyst or microporous layer (cf. Figure 4.2).
As can be seen, under the experimental conditions the CV seems to be strongly influenced by effects on the carbon surface not only of carbon black particles in the catalyst or microporous layers but by the carbon surfaces of the GDL material as well, since the redox couple around a potential of 0.5 V can be observed on the uncoated GDL. It is probably caused by surface oxide on carbon \(^{24}\). According to Kinoshita and Bett \(^{22}\) the carbon surface oxide contains electro-active quinoid groups which might account for the observed redox couples. In addition to the redox couple, Figure 4.2 shows an oxidation current with an onset around 0.9 V that must be attributed to carbon corrosion.
Comparable CVs to those depicted in Figure 4.1 have been recorded by McBreen et al. \cite{23} in their testing of different carbon support materials for Pt catalysts at 138 °C. Their CVs show an oxidative current maximum around 0.6 V and a maximum in the reductive current around 0.5 V, but the potential at which the carbon surface is oxidized and reduced appears to depend strongly on the type of carbon support used \cite{22}.

The measurement carried out on the sample held at 180 °C in Figure 4.1 suggests that most electrocatalytic activity is lost as there is no hydrogen or oxygen desorption evident in the CV. Comparison of CVs measured on different days with the same electrode (Figure 4.3) shows that the loss of catalytically active surface area is for the most part irreversible. In addition, the CVs show an irreversible change in shape, suggesting permanent changes in the structure of the catalytic surface and loss of catalyst or at least its electronic connection to the GDL.
The heightened currents in the double layer region might be a pseudo capacity due to the reversible oxidation and reduction of carbon surface groups as explained above. The increase of these currents might be caused by an increase of the carbon surface caused by degradation of the initially smoother carbon fibers of the GDL.

Figures 4.4 and 4.6 present mass spectrometric measurements corresponding to the CVs presented in Figure 4.1. Figure 4.4 shows the ion current signals for $m/z = 44$ corresponding to evolution of CO$_2$. At all temperatures in the range between 120 and 180 °C, formation of CO$_2$ can be observed at potentials above 0.3 V (cf. Figure 4.4). This suggests that carbon in the carbon paper of the GDL is oxidized leading to degradation.

All curves show a maximum of the ion current around 0.5 V. This maximum increases with increasing temperature up to 160 °C while the two last measurements show a decrease of the maximum. A second wave of CO$_2$ is detected at temperatures of 150 °C and above, the maximum appearing during the cathodic scan due to the delay time, but likely coinciding with reaching the vertex potential of 1.1 V. The onset of this second wave is between 0.9 and 1.0 V. The reason for the shape of the observed curves with their first wave of CO$_2$ formation is not easily apparent. There are two possible explanations which are not mutually exclusive:

The maximum around 0.5 V might be explained by carbon oxidation catalyzed by the Pt or the oxidation of pre-oxidized species like CO$_{ad}$ on the catalyst surface that were formed during the previous cycle, which could explain the low onset potential around 0.2 V. The carbon corrosion observed for the uncoated GDL in Figure 4.2, which occurs only at potentials above 0.9 V also indicates an involvement of the Pt in the CO$_2$ formation that can be observed at lower potentials.

A second explanation might be the adsorption of phosphate ions starting at a potential of 0.5 V [23,155–158] leading to a surface-blocking that hinders carbon oxidation in the potential window between 0.5 and 0.8 V [159]. The detection of CO$_2$ during the backward scan may simply be due to the ion current signal trailing behind the CO$_2$ released at the upper vertex potential (cf. Chapter 3).
Figure 4.4: MSCVs of m/z = 44 signal in nitrogen atmosphere on Pt black in the temperature range from 120 to 180 °C (scan rate 10 mV/s, 3rd cycle, baseline adjusted by subtraction of lowest value in the 0.1 – 0.5 V region).

There is also the question whether PTFE from the binder could be oxidized under the present conditions. MS measurements of the typical mass signals for HF, m/z = 19 and 20, as a
degradation product of the binder PTFE were not conducted on the Pt black electrode, but have been included during a later CV measurement in nitrogen atmosphere on a carbon supported PtRh electrode at 150 °C (cf. Figure 4.5). As the carbon supported electrodes contain PTFE binder as well, this should be an indicator if binder degradation is possible or not. As can be seen in Figure 4.5, the ion current for \( m/z = 19 \) stays constant apart from noise during the whole measurement. There is no obvious correlation of the \( m/z = 19 \) signal to the cyclovoltammetric scan, so formation of HF from the PTFE binder is highly unlikely.

![Figure 4.5: Faradaic current I and mass spectrometric ion current for \( m/z = 19 \) at 150 °C under nitrogen flow on PtRh/C (catalyst #VI) 0.92 mg/cm\(^2\) on GDL 10AA during a CV measurement (10 cycles) with a lower vertex potential of 0.0 V, an upper vertex potential of 1.1 V, a scan rate of 5 mV/s.](image)

Figure 4.6 shows the ion current signals for \( m/z = 2 \) corresponding to evolution of \( H_2 \) at low potentials. The CVs start at 0.5 V going in the anodic direction. The decline of the ion current up to the upper vertex potential as well as during most of the cathodic scan is due to hydrogen from preceding measurements still leaving the system. Hydrogen formed during measurements stays in the cell much longer than can be observed for \( CO_2 \), which is due to bad pumping efficiency of the turbo molecular pump for this gas. In order to be efficient the tips of the blades of the turbine must move faster than the average speed of the gas molecules it shall accelerate which is hardly the case for the very light and thus very fast hydrogen molecules.
An increase in the amount of hydrogen formed can be observed as the temperature of the cell is increased. It should be noted that this is true even for the highest temperatures where no or little catalytic activity of the Pt can be observed in the corresponding CV (cf. Figure 4.1). The onset potential for the H$_2$ formation increases with rising temperature. This effect has been observed before$^{[160]}$.

![Figure 4.6: MSCVs of m/z = 2 signal in nitrogen atmosphere on Pt black in the temperature range from 120 to 180 °C (scan rate 10 mV/s, 2$^{nd}$ cycle, baseline adjusted by subtraction of lowest value).](image)
4.2 CV and MSCV measurements of the ethanol oxidation reaction using a high ethanol feed concentration of 10.9 M on Pt black electro-catalyst in the temperature range of 120 to 160 °C.

CV and MSCV measurements of the ethanol oxidation reaction (EOR) on Pt black electro-catalyst in the temperature range of 120 to 160 °C have been recorded. The ethanol feed during the experiment was 10.9 M (500 g/L) aqueous ethanol solution at 25 µL/min (liquid at room temperature). The scan rate was 10 mV/s and only the 5th cycle of each measurement is depicted.

Figure 4.7: CV measurements (5th cycle) of ethanol oxidation in the gas phase on Pt black catalyst in the temperature range of 120 – 160 °C, feed 10.9 M aqueous ethanol solution 25 µL/min (liquid at room temperature), scan rate 10 mV/s.
Starting in the anodic direction the CVs show a slow onset of oxidative current between 0.4 and 0.5 V followed by an almost linear rise of the current with rising potential. In the cathodic sweep the oxidation current is generally a little higher than in the anodic sweep, down to a potential of ca. 0.5 V.

In the potential windows measured, no formation of an oxidation wave occurs, which is typically observed during EOR on Pt catalysts. Such an oxidation wave is formed when the ethanol oxidation current decreases again at potential higher that 0.8 V as a result of the formation of oxide species on the catalyst surface. This phenomenon will be further discussed in the conclusions of Chapters 5 and 6.

With the exception of the curve measured at 160 °C, an increase in temperature causes a steeper slope in the oxidation current. This drop in activity at 160 °C compared to the lower temperatures is probably caused by degradation effects on the electrode at high temperatures. To some degree this might also affect the curve measured at 150 °C which shows only a small change in activity compared to that at 140 °C. All curves were measured with the same working electrode in order of rising temperature.

An Arrhenius plot of the maximum in current density around 1.1 V (Figure 4.8) shows a linear trend only in the lower temperature region (120 to 150 °C). The maximum in current density was determined by taking the mean of the values of the cathodic sweep from the upper vertex potential down to a potential of 1.09 V. The given error is the standard deviation. A linear fit weighted for the error gives a negative slope \( m = (-1767 \pm 288) \text{ K} \). By multiplying with the universal gas constant \( R \) the apparent activation energy for the overall oxidation reaction can be calculated as \( E_a = (14.7 \pm 2.4) \text{ kJ/mol} \). A comparison to literature reference can be found in Chapter 4.4.
Figure 4.8: Arrhenius plot of the maximum current density (cf. Figure 4.7). Mean value and standard deviation of the values around the vertex potential ($E \geq 1.09$ V).

The mass spectrometric measurements MSCVs reproduced in Figure 4.9 show the mass spectrometric ion current for $m/z = 22$ corresponding to the $[\text{CO}_2]^{2+}$ fragment of CO$_2$. The MSCVs show a more pronounced influence of the temperature than the CV curves (cf. Figure 4.7). Disregarding the curve measured at 160 °C, which again shows a significant deviation from the general trend, a rise in temperature causes several changes in the shape of the curves: initially the slope of the ion current vs. potential shows a strong increase with increasing temperature. At temperatures of 140 °C and higher however a flattening of the curve can be observed starting at potentials around 0.75 V. This indicates a reduced selectivity for CO$_2$ formation under these potential conditions. Up to 140 °C the anodic and cathodic sweep are relatively similar in shape. At 150 and 160 °C however, a heightened CO$_2$ formation can be observed in the cathodic sweep between 0.5 and 0.25 V.
Figure 4.9: MSCVs corresponding to the CVs depicted in Figure 4.7. Ion current signal for \( m/z = 22 \) corresponding to \( \text{CO}_2 \).

Figure 4.10 and 4.11 show the MSCVs for \( m/z = 29 \) and 44 respectively. While the signal for \( m/z = 29 \) can correspond to acetaldehyde and ethyl acetate, the signal for \( m/z = 44 \) can correspond to either \( \text{CO}_2 \) or acetaldehyde. Measuring the much weaker \( m/z = 22 \) signal allows more reliable detection of \( \text{CO}_2 \) to be achieved.

The similar shapes of the \( m/z = 29 \) and 44 signals suggest that the ion current for \( m/z = 44 \) is in this case dominated by acetaldehyde and not \( \text{CO}_2 \). There are only small changes in the shape of the curves with rising temperature compared to the changes that can be observed in the curves of the \( m/z = 22 \) signal. The formation of acetaldehyde does not seem to be as strongly influenced by a change in temperature as the formation of \( \text{CO}_2 \). This suggests a lower activation barrier for acetaldehyde formation. Indeed, Andreadis et al. \(^{[161]} \) could confirm significantly lower apparent activation energies for the formation of acetaldehyde and acetic acid from ethanol compared to those required for the formation of \( \text{CO}_2 \). This stands to reason because of the high activation
barrier of the C-C bond splitting. An exception of the general trend is again the result of the measurement at 160 °C, which already showed a decline in performance in the CV measurements, probably due to catalyst degradation. The onset potential of the acetaldehyde formation around 0.4 V is similar to that of the formation of CO₂.

Figure 4.10: MSCVs corresponding to the CVs depicted in Figure 4.7 Ion current signal for m/z = 29 corresponding to acetaldehyde and ethyl acetate.
Figure 4.11: MSCVs corresponding to the CVs depicted in Figure 4.7. Ion current signal for $m/z = 44$ corresponding to CO$_2$ and acetaldehyde.

Figure 4.12 depicts the MSCV for $m/z = 61$ which corresponds to ethyl acetate formed by esterification of acetic acid and ethanol. As can be observed, there are significant amounts of acetic acid formed at all studied temperatures. As a general trend, an increase in temperature brings about an increase in the ion current for the signal. It has to be taken into consideration however, that the heightened temperature influences not only the formation of acetic acid, but might also significantly influence the esterification reaction and the evaporation of the detected ethyl acetate. The maximum in ion current appears in the backward scan around 0.7 V. It is likely that the maximum formation of acetic acid occurs at high potentials and the corresponding MS signal is delayed. The long delay between formation and detection suggest a much longer retention time in the system for ethyl acetate than for CO$_2$. 

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A direct comparison of the MSCV measurements for $m/z = 22$ and 44 in the presence and absence of ethanol (cf. Figure 4.13) shows that the carbon degradation and subsequent CO$_2$ formation observed in nitrogen atmosphere are small compared to the CO$_2$ formation observed during ethanol oxidation. A more serious concern is the instability of the baseline for the MSCV signals under ethanol/water vapor flow. Because of the large amount of these reactants entering the MS beside the EOR products, the baseline of the ion current signals is also significantly higher than in nitrogen. There also seems to be an influence of the temperature. For easier comparison of the MSCVs the baselines of Figure 4.9 to 4.12 have been corrected by subtracting the lowest value of the depicted cycle.
4.13: Direct comparison of MSCVs for $m/z = 22$ and 44 in nitrogen atmosphere and under ethanol/water.
4.3 CO$_2$ charge efficiency of the ethanol oxidation reaction on Pt black

CO stripping experiments have been conducted at 150 °C on Pt/C catalyst to quantify the correlation of the Faradaic current and the mass spectrometric ion current for $m/z = 22$. On base of this data CO$_2$ charge efficiencies (CCE) could be calculated (cf. Chapter 3).

Figure 4.14 shows the CCE during CV measurements on Pt black catalyst in the potential window of 0.0 V to 1.1 V in the temperature range between 120 °C and 160 °C. While the overall CCE on this catalyst is low, a significant increase with rising temperature can be observed. The CCE rises from ca. 10 % at 120 °C to 24 % at 160 °C.

![Figure 4.14: CO$_2$ charge efficiency on Pt black catalyst as a function of temperature.](image)

Figure 4.14: CO$_2$ charge efficiency on Pt black catalyst as a function of temperature.
4.4 Discussion and Conclusions

Measurements on carbon GDL electrodes sprayed with Pt black catalyst have been conducted. Background measurements under nitrogen flow in the temperature range between 120 °C and 180 °C show that the GDE shows signs of degradation, especially at temperatures of 160 °C and higher. These indicators are: 1) formation of small amounts of CO$_2$, detectable by mass spectrometry, that can only come from oxidation of the GDL as no carbon support for the catalyst is present, 2) changes in the shape of the CV and 3) loss of the features typical for Pt, which is reversible to some degree and thus points to an effect of the concentrated phosphoric acid electrolyte.

It could be shown that under the high temperature and concentrated phosphoric acid conditions, the carbon material of the GDL is not completely inert. As a consequence the measurements of ethanol oxidation were only conducted at temperatures up to 160 °C. The measurements using carbon supported catalysts, which will be presented in the following chapters, were restricted to 150 °C, as a compromise between improved kinetics at high temperature and a comparatively low degradation. No corrosion of binder material and subsequent HF formation could be detected. It could be shown that the amount of CO$_2$ formed by carbon corrosion is negligible compared to that formed in the EOR.

The shape of the CV curves measured at temperatures in the range of 120 to 160 °C with a 10.9 M (500 g/L) ethanol/water mixture shows an approximately linear current voltage dependence in the observed potential range. Usually a decrease of the ethanol oxidation current with increasing potential is observed after the onset of oxide formation on the Pt surface [60, 62, 64, 67, 69, 162]. The effect observed in the presented measurements is suspected to be connected to the high ethanol concentration and will be more closely discussed in Chapter 6.

The MSCVs show that significant amounts of the side products acetaldehyde and ethyl acetate are produced at all temperatures investigated, which is expected from previous measurements of the EOR. The CO$_2$ charge efficiency determined from the CVs and MSCVs for $m/z = 22$ is 10 % at 120 °C and 24 % at 160 °C. Wang et al. [79], who performed a cyclovoltammetric study of the EOR at several ethanol concentrations in 0.5 M H$_2$SO$_4$ on 20 % Pt/C reported a slightly decreasing average CO$_2$ current efficiency with rising temperature; between 7.9 % at 30 °C and
5.1 % at 60 °C with 0.01 M ethanol concentration. Other groups however saw an increase in the CO$_2$ current efficiency with rising temperature. Sun et al. [64] reported their highest steady-state CO$_2$ current efficiencies at their lowest measured potential of 0.48 V as between 4.6 % at 23 °C and 45% at 100 °C with 0.1 M ethanol and between 5.1 % at 23 °C and 86.9 % at 100 °C with 0.01 M ethanol. Likewise, Rao et al. [81] reported an increase of the CO$_2$ current efficiency with increasing temperature, exceeding 75 % at 90 °C. Andreadis et al. [161] reported CO$_2$ selectivities between around 5 % at 60 °C and 15 % at 90 °C in amperostatic experiments on PtRu/C catalyst with 1 M ethanol.

Considering the high temperature of the measurement cell, the values of the CO$_2$ charge efficiency in this study are somewhat lower than expected. So while their significant increase with rising temperature agrees with the literature, the rather low absolute values are probably caused by the high ethanol concentration [64, 79] and/or the low surface area that can be expected of the Pt black catalyst compared to carbon supported Pt [81].

An Arrhenius plot of the current value at the upper vertex potential of 1.1 V yields an apparent activation energy of $E_A = (14.7 \pm 2.4)$ kJ/mol.

Wang et al. [79] reported an activation energy of 32 kJ/mol for the overall reaction of 0.01 M ethanol in the temperature range of 30 to 60 °C. This value was determined via integrated charges measured during cyclovoltammetry. Even higher apparent activation energies were reported by Sun et al. [64], 40 to 50 kJ/mol depending on the potential applied in their chronoamperometric measurements (they measured at 0.48, 0.58 and 0.68 V) in the temperature range between 23 and 100 °C on 20 % Pt/C. They employed two different ethanol concentrations, 0.01 M and 0.1 M, and found slightly higher apparent activation energies using the lower concentration. Steady-state measurements on DEFCs have been published by Rao et al. [81] who reported an apparent activation energy of 31 kJ/mol at 0.1 M ethanol concentration and 0.6 V on a 40 % Pt/C catalyst in the temperature range between 30 to 90 °C, as well as by Colmati et al. [163] who reported 26 kJ/mol at 1 M ethanol concentration and 0.45 as well as 0.55 V on 20 % Pt/C catalyst between 70 and 100 °C.

Although the apparent activation energies determined by potentiostatic and potentiodynamic measurements are not directly comparable, there seems to be a clear trend towards a lower apparent activation energy for the overall EOR at higher ethanol concentrations. So the low
apparent activation energy found in this study could be caused by the high ethanol concentration. However, variation of mass transport conditions in different set-ups can have a big influence on the contribution of different reaction pathways and thus the overall apparent activation energy [64]. Thus another explanation might simply be a high contribution of side products produced via pathways with a low activation barrier on the Pt black catalyst, which is also apparent in the MSCVs.

The higher temperature range of these measurements could also be a possible explanation for the difference in the apparent activation energy, as an elevated temperature can influence the contribution of different reaction pathways. However, a study by Shimada et al. [164] on DEFC with CsH₂PO₄ solid electrolyte in the temperature range between 235 to 260 °C reported a high overall apparent activation energy for the EOR of around 60 kJ/mol.
5 Comparison of Pt black and carbon supported Pt at 150 °C

5.1 CV and MSCV measurements on 10 % Pt/C electro-catalyst in nitrogen atmosphere at 150 °C and comparison with Pt black.

The performance of carbon supported Pt catalyst at 150 °C was studied and compared to the behavior of the Pt black catalyst at that temperature (as presented in Chapter 4).

Figure 5.1 shows the CVs and corresponding MSCVs for mass to charge ratio 44 in nitrogen atmosphere at 150 °C. The upper vertex potentials is 1.1 V on Pt black, on Pt/C however, a slightly lower upper vertex potential of 0.9 V had to be chosen to avoid degradation of carbon.

The CVs are similar in shape, but despite its higher loading, Pt black provides significantly lower currents due to its lower active surface area. The features of the CVs are not very well defined. In the anodic scan, a broad oxidation wave can be observed in the hydrogen desorption area, as well as another oxidation wave around 0.6 and 0.65 V respectively, which could be linked to the CO₂ production observed in the MS measurements. Carbon oxidation begins at a potential of ca. 0.85 V. In the cathodic scan there is a peak around 0.8 V with Pt black and a shoulder around 0.7 V with Pt/C which probably corresponds to oxygen desorption from the Pt surfaces. A second wave can be observed around 0.4 V. While this is a rather high potential for hydrogen adsorption it might be possible considering the high temperature. Another explanation could be desorption of adsorbed phosphates or a contribution of both processes.

The MSCV for $m/z = 44$ which corresponds to CO₂ formation shows no fundamentally different behavior between the two GDEs. Both Pt black and Pt/C show a peak in CO₂ formation at 0.6 and 0.65 V respectively and the onset of a second peak at ca. 0.85 V which reaches its maximum during the backward scan.

There seems to be no major difference in the oxidation of carbon paper and carbon support under these conditions. The differences in the MSCVs are likely due to the higher surface area of the carbon support. Carbon degradation behavior might also be related to the active surface area of the catalyst as has been suggested by Passalacqua et al.\[24\].
Figure 5.1: CV and MSCV for $m/z = 44$ on Pt black (a, b) and Pt/C (c, d) in nitrogen atmosphere at 150 °C (scan rate 10 mV/s).

Calculation of the CCEs during CV measurements on Pt/C catalyst in the potential window of 0.0 V to 0.9 V at temperatures of 150 °C and 170 °C give values of 79 % at 150 °C and 90 % at 170 °C. Since especially at high potentials the current efficiency is expected to be low [33,81] no direct comparison of the overall CCEs measured on supported and unsupported Pt catalyst can be made due to the different potential windows used in the measurements.

Still, a more porous catalyst with higher active surface area can have a positive influence on the CO$_2$ current efficiency as it results in a longer dwell time of the reactants, thus increasing the chances for a complete oxidation. These results are in agreement with measurements by Rao et al. [81] who reported a lower CO$_2$ current efficiency on unsupported Pt compared to Pt/C and PtSn/C catalysts.
5.2 CV and MSCV measurements of the ethanol oxidation reaction on 10 % Pt/C electro-catalyst at 150 °C using a high ethanol feed concentration of 10.9 M and comparison with Pt black.

CVs and MSCVs for mass to charge ratios m/z = 22, 44, 29 and 61 have been measured at 150 °C for the EOR on Pt black (cf. Figure 5.2) and Pt/C (cf. Figure 5.3) electro-catalysts. Note that for the measurements on the carbon supported catalyst a smaller potential window had to be chosen than for the measurements on Pt black to avoid oxidative degradation.

As already mentioned above the mass spectrometric ion current for mass to charge ratio 22 corresponds to the [CO₂]²⁺ fragment of CO₂. An analysis of the other mass spectrometric signals is less straightforward since the signals for m/z = 44 and 29 can be assigned to more than one oxidation product. While acetaldehyde has two major fragments – [C₂H₄O]⁺ and [CHO]⁺ – with the mass to charge ratios of 44 and 29 respectively, the carbon dioxide fragment [CO₂]⁺ is also assigned to m/z = 44. Ethyl acetate which is formed by esterification of acetic acid and ethanol corresponds to m/z = 61 but can also contribute to m/z = 29.

Some considerations have to be taken into account concerning the formation of ethyl acetate. First, it is only formed after a partial electrocatalytic oxidation of ethanol to acetic acid or to an adsorbed acetyl species and, second, the esterification might take place at the catalyst surface as a potential dependent electrochemical reaction \[^{[57,58]}\], but it could also proceed as an acid-catalyzed equilibrium reaction that occurs independently of the applied potential. In the latter case corresponding MS signals might be, as observed in the experiment, slightly delayed and, more importantly, have a very slow decline if the rate of lowly volatile acetic acid formation at high potential is much faster than the following esterification. Such slowly declining signals are not expected of the more volatile ethyl acetate is formed within an electrochemical surface reaction, so that the results support a predominant formation of ethyl acetate via the esterification route in contrast to the situation reported for low temperature measurements \[^{[57,58]}\]. In spite of the distorted MS signals some conclusions may be drawn by qualitative comparison of the measurements.
5.2.1 Comparison of the Faradaic currents

A comparison of the Faradaic currents measured on both catalysts shows little difference in the overall shape of the CV curves.

On Pt black catalyst the measured onset of the oxidative current is 0.38 V. Scanning in anodic direction from this potential the slope of the curve increases until it reaches a maximum of 0.06 A/cm² / V at a potential of 0.57 V. After this the slope shows a slight decline until reaching the upper vertex potential of 1.1 V.

On Pt/C catalyst the onset occurs at a lower potential of 0.29 V. The slope of the curve increases up to 0.1 A/cm² / V at a potential of 0.70 V and then stays constant until reaching the upper vertex potential of 0.90 V. On the carbon supported catalyst the maximum current density measured is 68 mA/cm² at the upper vertex potential, compared to 27 A/cm² at the same potential on the Pt black catalyst. Also the capacitive currents that can be observed at lower potentials are much higher on the Pt/C catalyst due to its higher active surface.

5.2.2 Mass spectrometric measurements on Pt black electro-catalyst

The mass spectrometric measurements on Pt black catalyst show an increase in ion current for \( m/z = 22 \) that coincides roughly with the onset of the Faradaic oxidation current. At a potential of ca. 0.75 V however, the slope starts to flatten significantly, indicating a decrease of CO₂ current efficiency at higher potentials, since there is no sign of a comparable decrease in the Faradaic current or the other ion currents.

It is known that at potentials higher than 0.8 V the Pt surface is increasingly covered with chemisorbed oxygen, which might hinder the complete oxidation to CO₂, but still facilitate the incomplete oxidation pathways forming acetaldehyde and acetic acid \(^{[79]}\). The high temperature could explain a slightly earlier onset of this process.

The similarity in shape of the ion current vs. potential curves of \( m/z = 44 \) and 29 give rise to the assumption that the contribution of acetaldehyde to the \( m/z = 44 \) signal outweighs the contribution of CO₂. This indicates a significant formation of acetaldehyde on this catalyst. The fact that the decrease of ion current of \( m/z = 22 \) at potentials above 0.75 V has little impact on the
Faradaic current is a further sign that the complete oxidation to \( \text{CO}_2 \) is only a side reaction under these conditions.

Finally the curve of \( m/z = 61 \) indicates formation of ethyl acetate with the onset of an increase of the ion current at a potential of \( \text{ca.} \ 0.5 \ \text{V} \).

There is no indication that the increased formation of acidic acid leads to a decrease in acetaldehyde formation.

### 5.2.3 Mass spectrometric measurements on Pt/C catalyst

On carbon supported Pt catalyst the curve for \( m/z = 22 \) shows a steady increase of ion current with rising potential with an onset of \( \text{ca.} \ 0.5 \ \text{V} \). Even keeping in mind the smaller potential window, there seems to be no flattening of the curve at potentials higher than 0.75 V as can be observed on Pt black catalyst. The curve for \( m/z = 61 \) however indicates formation of ethyl acetate starting at a potential around 0.5 V. The similarity of the shape of the curve for \( m/z = 44 \) with 22 as well as \( m/z = 29 \) with 61 suggests that the amount of acetaldehyde produced is small and its contribution to the 44 and 29 signal outweighed by the bigger contributions of \( \text{CO}_2 \) and ethyl acetate respectively.

The mass spectrometric measurements on Pt/C catalyst indicate that acetic acid and \( \text{CO}_2 \) are formed simultaneously between the potentials of 0.5 V and 0.9 V.
Figure 5.2: CV and MSCVs for mass to charge ratios $m/z = 22, 44, 29$ and $61$ of EOR in the gas phase at $150^\circ$C on Pt black electro-catalyst at 10.9 M ethanol feed concentration.
Figure 5.3: CV and MSCVs for mass to charge ratios \( m/z = 22, 44, 29 \) and 61 of EOR in the gas phase at 150 °C 10 % Pt/C electro-catalyst at 10.9 M ethanol feed concentration.
5.3 Discussion and Conclusions

A comparison of GDEs with Pt black catalyst and carbon supported catalyst under nitrogen at 150 °C reveals a similar formation of CO\textsubscript{2} from carbon corrosion in the region around 0.6 V in the anodic scan. This peak might be connected to the oxidation of preadsorbed species on the catalyst surface, as it appears at a potential similar to that of the CO oxidation peak during CO stripping experiments (cf. Chapter 3). However, when carbon support is present, a more distinct CO\textsubscript{2} formation can be detected, starting at lower potentials. This is likely due to the larger surface of the support compared to the GDL fibers. In any case the maximum of the ion current for \textit{m/z} = 44 seems to always appear around 100 mV into the cathodic scan.

As was the case on Pt black catalyst the oxidation of 10.9 M ethanol on carbon supported Pt at 150 °C show an approximately linear increase of the current with rising potential and a nearly identical decline in the anodic scan. Several DEMS studies have been conducted on the bulk oxidation of ethanol on platinum \cite{43,57,60,62,64,67,69,82,118,119,162,165,166}. Generally the CV shows two oxidation waves, one with the maximum around 0.8 V \cite{60,62,64,67,69,162}, and the second with the maximum around 1.3 V \cite{67,69,162}. The decrease of the current at potentials around 0.8 V is usually assigned to partial blocking of the Pt surface with surface oxide \cite{64}.

Under some conditions however, the maximum of the first oxidation wave is shifted to a higher potential and nearly linear current over potential curves have been reported up to potentials of 0.8 V \cite{60,118,119}, 0.9 V \cite{166} or even 1.0 V \cite{63}. Rao \textit{et al.} \cite{81,82} measured CV curves similar to the one presented in above with a Nafion® \cite{81} and AEM \cite{82} fuel cell set-up operated in half cell mode. In the case of the Nafion® fuel cell, the near linear CV curve could only be observed at 1 M ethanol concentration, while a 0.1 M ethanol concentration leads to a CV with an oxidation wave with a maximum around 0.8 V. A near linear CV curve has also been reported on sputter deposited Pt in 0.1 M ethanol and 0.1 M KOH electrolyte up to a potential of 1.1 V \cite{57}.

A qualitative analysis of the MSCVs indicates that significant amounts of acetaldehyde are formed on the Pt black catalyst, but not on carbon supported Pt. In both cases ethylacetate is formed as one of the main product besides CO\textsubscript{2}. One reason for this is a higher dispersion and electrochemically active surface area of the Pt/C catalyst compared to the Pt black catalyst. Rao \textit{et al.} \cite{81} reported lower CCEs for lower catalyst surface areas, but also for unsupported Pt
catalyst of the same electrochemically active surface area as supported Pt catalyst. They explained that as an effect of a longer residence time of the ethanol over the catalyst surface in the thicker catalyst layer of supported catalysts, which leads to a higher change for acetaldehyde to be further oxidized to CO$_2$ or ethyl acetate and acetic acid. In this way the more voluminous catalyst structure can have a similar effect as a slower flow\textsuperscript{[64]} rate as both influence the mass transport of the reactant.
6 The influence of ethanol concentration on the ethanol oxidation reaction

The previous EOR measurements using an ethanol feed with a concentration of 10.9 M ethanol show significant differences compared to EOR measurements done in liquid phase measurements. On the one hand the temperature and mass transport conditions are not the same, but on the other hand the high ethanol concentration is another factor to impact the reaction. In most literature references far lower ethanol concentrations up to 1 M ethanol are used. Though a higher water content in the ethanol feed impedes the MS measurement via capillary to a certain extent, a 1 M ethanol feed has been found to be feasible.

6.1 CV and MSCVs of the ethanol oxidation reaction on Pt/C using 1 M ethanol

Reducing the ethanol concentration in the aqueous feed leads to significant changes in the corresponding CV and MSCV measurements (cf. Figure 6.1). The figure shows the CV and MSCVs for mass to charge ratios $m/z = 22, 44, 29$ and $61$ on a 10 % Pt/C catalyst of comparable loading at 150 °C and an ethanol feed concentration of 1 M.

The most obvious difference in the CV compared to the measurements with 10.9 M ethanol (cf. Figure 5.3) is the formation of an oxidation wave with a maximum at ca. 0.5 V. Apparently, with 1 M ethanol concentration the water content in the gas phase is high enough to result in oxide covered catalyst surfaces at potentials above 0.5 V. This leads to an inactivation and the resulting decrease in current that is typically observed in aqueous solutions \[60,62,64,67,69,162\].

Another point of interest is the fact that at potentials where the current is not decreased by a blockage of catalytic surface, the current densities measured are similar to those measured at the high ethanol concentration. Since both measurements were carried out at an ethanol feed rate of 30 µL/min, the current measured at low concentration might be expected to be significantly smaller than at high concentration. The similar currents measured when feeding either 1 or 10.9 M ethanol suggests that even at the lower concentration the ethanol at the anode is not
depleted during the CV measurement and the current is still limited by the available catalyst surface and not the educt concentration.

The MSCV measurements using 1 M ethanol feed show a high level of noise that is due in part to the higher water content of the sampled gas and in part to the smaller concentration of products. Nonetheless, the similar shape of the MSCV curves for $m/z = 22$ and 44 that also closely follow the shape of the CV curve, suggest that under these conditions a significant amount of the reacting ethanol is indeed completely oxidized to CO$_2$. The MSCV for $m/z = 29$ and 61 are not as conclusive because of their high noise level, but the signals are generally weaker than the corresponding measurements at high ethanol concentration and the curves do not exhibit features of the CV.
Figure 6.1: CV and MSCVs for mass to charge ratios m/z = 22, 44, 29 and 61 of EOR in the gas phase at 150 °C 10 % Pt/C electro-catalyst at 1 M ethanol feed concentration.
6.2 The effect of the ethanol concentration on CVs of the ethanol oxidation reaction on Pt/C and PtRh/C

Figures 6.2 and 6.3 depict CV curves for the EOR with 5 M and 1 M ethanol on Pt/C and PtRh/C catalyst respectively. In this series of measurements the ethanol oxidation wave using 1 M ethanol appears at a higher potential compared to the measurement presented in Figure 6.1. However it can be seen that even at a intermediate ethanol concentration of 5 M with both the Pt/C and the PtRh/C catalyst the peak in the oxidation current is lost and instead the near linear shape of the CV curve appears.

Figure 6.2: CVs on 10 % Pt/C (catalyst II), 5 M ethanol 1.47 mg/cm² metal loading, 1 M ethanol 1.48 mg/cm² metal loading, scan rate 10 mV/s.
Figure 6.3: CVs on 10 % PtRh/C (catalyst III), 5 M ethanol 1.05 mg/cm² metal loading, 1 M ethanol 1.04 mg/cm² metal loading, scan rate 10 mV/s.

To see if an oxidation wave occurs at higher ethanol concentrations than 1 M as well, the upper vertex potential has been increased in 0.1 V steps during CV measurements on 7 % PtRh/C at different ethanol concentration until an oxidation wave could be observed. Figure 6.4 shows the resulting CVs at 3, 5, and 7 M ethanol concentration. The peaks of the oxidation wave in both the anodic and the cathodic scan are shifted to significantly higher potentials at higher ethanol concentrations. This effect results in the near linear CV curves that can be observed during the previously presented EOR obtained with 10.9 M ethanol (cf. Chapter 5).
Since the formation of the oxidation wave is connected to the onset of oxide formation on the Pt surface, the shift in potential is likely due to the low concentration of water and the high concentration of ethanol. It can be hypothesized that as both compounds compete for adsorption sites, the higher ethanol to water ratio leads to an increased adsorption of ethanol instead of water, which shifts the formation of the oxide layer on the Pt to higher potentials.

A plot of the peak potentials in the forward and backward scan as well the onset potentials of the oxidation wave during the backward scan suggest a near linear increase in the potentials when increasing the ethanol concentration in the liquid feed. For comparison the peak potentials of the CV measurement on 10 % Pt/C at 1 M ethanol concentration as presented in Figure 6.1 has been
added. The peak potentials measured at 1 M are a little lower than the general trend of the other measurements would suggest, which could be an effect of the different catalyst.

Figure 6.5: Peak potentials and potentials of the onset of the oxidation wave during the backward scan observed in CVs on 7.35 % PtRh/C (catalyst VI) with a metal loading of 0.92 mg/cm² at ethanol concentrations of 3, 5, and 7 M, and on 10% Pt/C with a metal loading of 1.31 mg/cm² at 1 M ethanol concentration (cf. Figure 6.1).
6.3 Discussion and Conclusions

CV measurements on Pt/C catalyst using 1 M ethanol show the typical oxidation wave in the CV curve due to the oxidation and inactivation of the Pt surface at high potentials. A qualitative comparison of the MSCVs to those measured with 10.9 M ethanol feed suggests that at the lower concentration more CO$_2$ and less of the side products are formed during the EOR than at high ethanol concentration. This is in agreement with findings in the literature $^{[64,72,73,79,81]}$.

CV measurements at three different ethanol concentrations on PtRh/C catalyst show that the linear shape of the CV curve observed at high ethanol concentrations is an effect of a shift of the oxidation wave to a higher potential at these high concentrations. If a high enough upper vertex potential is chosen, an oxidation wave can be observed at an ethanol concentration as high as 7 M. In the observed range of 3 to 7 M the potentials of the features in the CV curve seem to increase linearly with the ethanol concentration in the liquid feed. In comparison, the peak potentials of the EOR on Pt/C at 1 M are slightly lower than expected, but might roughly follow the same trend.
7 Chronoamperometric measurements

7.1 Chronoamperometric (CA) and MSCA measurements on Pt/C catalysts at 150 °C for ethanol feed concentrations of 10.9 M and 1 M

Chronoamperometric measurements have been performed for 600 s following a potential jump from 0.1 V to 0.2, 0.3, 0.4, 0.5 and 0.6 V respectively at ethanol feed concentrations of 10.9 and 1 M (cf. Figure 7.1). The current responses at the two concentrations show a very different behavior.

![Figure 7.1](image)

Figure 7.1: Chronoamperometric measurements on 10 % Pt/C following a potential jump from 0.1 V to 0.2, 0.3, 0.4, 0.5 and 0.6 V respectively at ethanol feed concentrations of a) 1 M (1.31 mg Pt/cm², 150 °C) and b) 10.9 M (1.25 mg Pt/cm², 140 °C).

In the measurements with the higher ethanol concentration of 10.9 M the initial capacitive current declines quickly until a comparatively stable Faradaic current is reached. This current increases
with rising step potential. At 0.5 and 0.6 V a slow decline of the current can be observed after ca. 500 s.

The measurements with 1 M ethanol solution show some noise, but nonetheless, some clear trends are visible in the chronoamperometric curves shown: after the initial capacitive current a shoulder can be observed where the reaction is not yet limited by the mass transport of ethanol to the electrode. The shoulder is followed by a slow decline of the current until a current limit is reached that is strongly influenced by fluctuations in the ethanol feed. An exception is the measurement at 0.2 V which shows a very stable current. There is an increase of the limiting current when the potential is increased from 0.2 to 0.3 V, but a stagnation or even decrease of the limiting currents at higher potentials.

A comparison of the limiting currents using 10.9 M and 1 M ethanol show much higher currents at the lower concentration at potentials of 0.2 and 0.3 V. At higher potentials however the currents are comparable or even lower than those measured at the higher concentration. This is probably due to the inactivation by oxide species that can also be observed in the CVs with 1 M ethanol (cf. Figure 6.1).

The corresponding mass spectrometric measurements (Figures 7.2 and 7.3) show high noise and fluctuating signals for \( m/z = 29 \), but there is no clear increase of the ion current visible as a result of the potential jump at 300 s, which suggests little formation of acetaldehyde. In the case of \( m/z = 61 \), an increase of the ion current at 300 s can be observed at potentials of 0.4 V and above using 10.9 M ethanol and 0.5 V and above using 1 M ethanol. This suggests significant formation of ethyl acetate under these experimental conditions.

While using 10.9 M ethanol, significant amounts of CO\(_2\) can only be observed at potentials of 0.4 V and above, with 1 M ethanol feed, the highest CO\(_2\) signals can be observed at 0.3 and 0.4 V. With both ethanol concentrations there is a high congruence between \( m/z = 44 \) and 22 ion current signals, while as already stated above, the \( m/z = 29 \) signal appears mostly featureless. This indicates that little or no acetaldehyde is formed at both concentrations and all measured potentials.
Figure 7.2: MSCAs for m/z = 22, 44, 29, and 61, using 10.9 M (500 g/L) EtOH/H$_2$O, flow rate (liquid) 30 µL/min, 140 °C, potential jump: 0.5s at 0.0V, 300s at 0.1V, 600s at the potential given in the legend, 10 % Pt/C catalyst 1.25 mg Pt/cm$^2$. 
Figure 7.3: MSCAs for m/z = 22, 44, 29, and 61, using 1 M EtOH/H₂O, flow rate (liquid) 30 µL/min, 150 °C, potential jump: 0.5s at 0.0V, 300s at 0.1V, 600s at the potential given in the legend, 10 % Pt/C catalyst 1.31 mg Pt/cm².

There is a clear increase in the m/z = 61 ion current signal with rising potential using 10.9 M ethanol, suggesting that ethyl acetate production is significant and that only at low potentials of 0.2 and 0.3 V no or little ethyl acetate is formed. With 1 M ethanol, this trend is not as apparent. The ethyl acetate signals are generally lower, with little or no production of ethyl acetate at 0.2 and 0.3 V, low signals at 0.4 and 0.5 V and a significant increase only at 0.6 V.
7.2 CA and MSCA measurements on Pt/C and PtRh/C catalysts at 150 °C for ethanol feed concentrations of 10.9 M, 5 M and 1M

CA measurements have been performed at 150 °C on carbon supported Pt and PtRh electro-catalysts prepared in the laboratory. After a starting potential of 0.14 V held for 5 minutes, the current responds at 0.19 V, 0.39 V, 0.59 V and 0.79 V were recorded over a time of 15 minutes. To study the influence of the ethanol concentration, three different aqueous ethanol solutions have been used in the feed: 10.9 M, 5 M and 1 M. The flow of the liquid feed was adjusted so that gas flow was approximately the same at each concentration.

Table 7.1: Volume and concentration of ethanol and water in the gas phase assuming an ideal gas.

<table>
<thead>
<tr>
<th>c_{\text{EtOH}}</th>
<th>M</th>
<th>1</th>
<th>5</th>
<th>10.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ (measured)</td>
<td>mg/µL</td>
<td>0.993</td>
<td>0.933</td>
<td>0.894</td>
</tr>
<tr>
<td>mass concentration EtOH</td>
<td>mg/µL</td>
<td>0.046</td>
<td>0.23</td>
<td>0.501</td>
</tr>
<tr>
<td>mass concentration H₂O</td>
<td>mg/µL</td>
<td>0.947</td>
<td>0.703</td>
<td>0.393</td>
</tr>
<tr>
<td>c_{\text{H₂O}}</td>
<td>mmol/µL</td>
<td>0.0526</td>
<td>0.0391</td>
<td>0.0218</td>
</tr>
<tr>
<td>c_{\text{EtOH}} (in gas phase)</td>
<td>mol/L(g)</td>
<td>8.33·10⁻⁴</td>
<td>5.06·10⁻³</td>
<td>1.49·10⁻²</td>
</tr>
<tr>
<td>flow (liquid)</td>
<td>µL/min</td>
<td>23.24</td>
<td>28.26</td>
<td>38.06</td>
</tr>
<tr>
<td>c_{\text{H₂O}} (in gas phase)</td>
<td>mol/L(g)</td>
<td>4.38·10⁻²</td>
<td>3.96·10⁻²</td>
<td>2.98·10⁻²</td>
</tr>
</tbody>
</table>

The gas diffusion electrodes used for the CA measurements are given in Table 7.2. In the cases where the same electrode was used for measurements at two ethanol concentrations, the measurement at lower ethanol concentration was conducted prior to that at the higher concentration.
Table 7.2: Working electrodes and their catalyst loadings for each CA measurement at the given ethanol concentration.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Ethanol concentration</th>
<th>Electrode</th>
<th>Catalyst loading (metal)</th>
<th>Pt loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>Type</td>
<td>M</td>
<td></td>
<td>mg/cm²</td>
</tr>
<tr>
<td>II</td>
<td>10%Pt/C</td>
<td>1.0</td>
<td>A</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>B</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td>B</td>
<td>1.47</td>
</tr>
<tr>
<td>III</td>
<td>PtRh/C: 5.14% Pt, 4.95% Rh</td>
<td>1.0</td>
<td>C</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>D</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td>C</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 7.4 summarizes the results for all three concentrations and for both Pt/C and PtRh/C catalysts. The current response recorded is for a potential jump from 0.14 V to the respective potentials given in the legend. To facilitate comparison, the current density is given per mg catalyst. A comparison of both electrodes shows similar behaviors at the different ethanol concentrations.

Notably, with the 5 M ethanol (Figures 7.4 c and d) a constant current is achieved. This has positive implications for the fuel cell efficiency that can be expected in this concentration range.

Especially the PtRh/C catalyst shows the best performance at this ethanol concentration. In contrast, on the Pt/C catalyst the currents are basically the same for all measured concentrations except at the highest potential of 0.79 V. At this potential the current on Pt is initially significantly higher than that measured with 5 M ethanol. However it is observed to decrease during the measurement to a value similar to that observed using 5 M ethanol.

At 1 M ethanol concentration (Figure 7.4 e and f) the measured currents are less stable than at the other concentrations. This is especially salient for the highest measured potential of 0.79 V, but can also be observed to a lesser degree in the measurement at 0.59 V. There are several possible reasons for this observation:
Figure 7.4: Current densities (per geometrical electrode surface) corrected for catalyst (metal) loading of GDEs with PtRh/C catalyst (a, c, e) and Pt/C catalyst (b, d, f) measured at different ethanol concentrations (10.9 M (a, b), 5 M (c, d), 1 M (e, f)) after a potential jump from 0.14 V to potential given in the legend.

1) That the ethanol feed is not as constant as at the other concentrations as the high water content of the 1 M ethanol/water mixture could lead to condensation in the feed. This could lead to a temporary depletion of ethanol at the catalyst surface and thus to a decrease of the measured current. The $\lambda$ values presented in Table 7.3 show that at 1 M the amount of ethanol supplied to the electrode is only slightly over-stoichiometric while at the other ethanol concentrations a large excess of ethanol is present.

2) That the high coverage of the catalytic surface with oxygen species at high potential and high water content leads to a blocking of large amounts of the catalyst surface for ethanol adsorption,
with fast oxidation and desorption occurring wherever ethanol adsorbs to the catalyst surface, leading to the observed current spikes.

Table 7.3: \( \lambda \) values calculated for the three concentrations assuming six transferred electrons per ethanol molecule.

<table>
<thead>
<tr>
<th>( c_{\text{EtOH}} )</th>
<th>Flow (liquid)</th>
<th>Ethanol flow</th>
<th>Theoretical current</th>
<th>Highest measured current</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>( \mu \text{L/min} )</td>
<td>( \text{mol/s} )</td>
<td>A</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>23.24</td>
<td>( 0.39\cdot10^{-6} )</td>
<td>0.22</td>
<td>0.16</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>28.26</td>
<td>( 2.36\cdot10^{-6} )</td>
<td>1.36</td>
<td>0.15</td>
<td>9.1</td>
</tr>
<tr>
<td>10.9</td>
<td>38.06</td>
<td>( 6.91\cdot10^{-6} )</td>
<td>4.00</td>
<td>0.14</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Apart from the ‘noise’ using 1 M ethanol, the performance is comparable to that with 5 M ethanol on both catalysts for all but the highest potential. The decrease of performance at high potential at 1 M ethanol concentration is in agreement with the CV measurements at that concentration which show an oxidation wave with a decline in current at potentials above ca. 0.5 V. When looking at the results obtained using 10.9 M and 5 M ethanol on the other hand, the reaction rate only increases with rising potential in the observed potential range.

Considering the measured potentials, the current measured at 0.19 V under steady state conditions is negligible on both types of electrodes. 0.39 and 0.59 V step potentials yield stable currents for both electrodes and all three ethanol concentrations, with the exception of the PtRh electrode at 1 M ethanol. A step potential of 0.79 V finally shows the best performance on both catalysts at high ethanol concentrations while the current density at that potential declines at the 1 M ethanol feed.

To see how the variation of electrode potential and ethanol concentration impact the product distribution on both types of catalyst, the mass spectrometric ion currents for \( m/z = 22, 44 \) and 61 detected during the CA measurements have been analyzed. Figure 7.5 shows the integrated charges obtained from the Faradaic current over time as well as the mass spectrometric ion currents over time.
Comparing the \( m/z = 22 \) and 44 charges directly it can be observed that at the low ethanol concentrations (Figure 7.6) the charges calculated from both ion current signals are mostly congruent. At the 10.9 M ethanol concentration however, the charges of \( m/z = 44 \) are significantly higher than would be expected when looking at the \( m/z = 22 \) charges (Figure 7.7).
This disparity between the observed charges indicates acetaldehyde formation as acetaldehyde contributes to the $m/z = 44$ charge, but not to the $m/z = 22$ charge.

The observed effect of the high ethanol concentration on the product distribution is stronger on the PtRh catalyst. Here acetaldehyde formation can be observed to start at a lower potential. In addition, the differences between the charges are consistently bigger in the presence of Rh compared to the pure Pt catalyst.

Figure 7.6: Direct comparison of the mass spectrometric charges for $m/z = 22$ and 44, with 1 M and 5 M ethanol.
Figure 7.7: Direct comparison of the mass spectrometric charges for m/z = 22 and 44, with 10.9 M ethanol.

The plot of the m/z = 61 charges (Figure 7.5 b) shows a clear pattern for both catalysts. It can be observed that ethyl acetate is formed preferably at high concentrations and high potentials. The amount of ethyl acetate detected is generally small at 0.39 V. At higher potentials it strongly depends on the ethanol concentration.

At most measurement conditions there seems to be more ethyl acetate produced at the PtRh electrode than at the Pt electrode. Indeed, when divided by the corresponding Faradaic charge the amount of ethyl acetate produced is higher on the PtRh catalyst compared to the Pt catalyst at potentials of 0.59 and 0.79 V (cf. Figures 7.8 and 7.9). While the effect is comparatively small at 1 and 5 M ethanol concentration, there is a huge difference at the highest measured concentration of 10.9 M. It is possible that under conditions of high potential and ethanol concentration the presence of Rh as an OH$_{ad}$ donor actually promotes the formation of acetic acid/ethyl acetate. It is
however more likely that a bigger contribution is due to the fact that the higher ethanol concentration would lead to a shift in the ratio of acetic acid and ethyl acetate produced. Thus, even if the total amount of both oxidation products stayed the same, more ethyl acetate would be detected.

Figure 7.8: Ratio of the charge calculated from the mass spectrometric ion current of \( m/z = 61 \) and the Faradaic charge on \( \text{Pt/C} \) and \( \text{PtRh/C} \) catalyst at different ethanol concentrations measured at a potential of 0.59.
Looking at the plot of the Faradaic charge (cf. Figure 7.5 d) it can be observed that at a potential of 0.19 V no significant charge is measured on both catalysts and with all concentrations. At a potential of 0.39 V the ethanol concentration seems to have no big influence on the Faradaic charge, but the Pt electrodes show better overall performance than the PtRh electrodes.

The small impact of the concentration can be evaluated in a magnification (cf. Figure 7.10 on the left). It can be observed that the performance at 10.9 M ethanol is lowest on both catalysts. The values for 1 M and 5 M ethanol however are similar for either catalyst, with a slightly higher Faradaic charge value with 1 M ethanol on Pt, and with 5 M ethanol on PtRh.

At a potential of 0.59 V most of the measured Faradaic charges are still similar. The exception is the charge measured at the 10.9 M ethanol concentration on the PtRh catalyst (cf. Figure 7.5 d). The right graph of Figure 7.10 shows a magnification of the other charge values. In the case of the Pt catalyst the measured charge increases slightly with increasing ethanol concentration at this potential. On the PtRh catalyst the measured charge is higher at 5 M ethanol concentration compared to 1 M concentration, but decreases strongly at 10.9 M.
Finally, the biggest differences between the charges measured on the two catalysts can be observed at the highest measured potential of 0.79 V (cf. Figure 7.5 d). At a 1 M ethanol concentration a similar charge is measured on the two catalysts. On the Pt catalyst there is a big increase in the charge when changing to a 5 M ethanol solution, and again a smaller increase when going to 10.9 M. On the PtRh catalyst the charge measured at 5 M ethanol concentration is almost twice as high as with 1 M, but at 10.9 M it decreases again to a value close to that measured using 1 M ethanol.
Figure 7.11: Charge per geometric electrode area over potential and ethanol concentration.

Figure 7.12: Charge per catalyst (metal) loading over potential and ethanol concentration.
The difference between the two catalysts at 0.39 V can partly be attributed to the higher loading of the Pt catalyst. When correcting the measured charge per geometric electrode area (Figure 7.11) for the total catalyst loading (Figure 7.12), the Pt catalyst still shows a slightly better performance than the PtRh catalyst at 0.39 V, but the difference decreases. Finally, if scaled in relation to the amount of Pt in the catalyst (Figure 7.13) Pt and PtRh show approximately the same performance at 0.39 V.

Figure 7.14 shows a plot of the CO$_2$ charge efficiencies of the CA measurements over the potential. The CO$_2$ charge efficiencies were calculated from the integrated Faradaic currents and mass spectrometric ion currents for m/z = 22 over the time of the measurement. Measurements at 0.19 V as well as the measurement at 0.39 V on PtRh/C at 10.9 M ethanol concentration were not evaluable because the low activity at this potential leads to a low signal to noise ratio for the mass spectrometric signals. The measured CCEs vary strongly with measurement conditions, ranging from 25% up to 75%.
As a general trend it can be observed that the CO\(_2\) efficiencies decrease at higher potential, with the exception of the measurements on Pt/C at 5 M ethanol concentration were the CO\(_2\) efficiency can be observed to increase with increasing potential. According to the literature the CCE can be expected to decrease with increasing potential which is generally explained by a lower tendency for C-C bond breaking at higher potentials as well as the increasing coverage with oxide species which leads to a lower availability of pairs of adsorption sites necessary for C-C bond breaking.

At high ethanol concentrations the CCE is higher on PtRh/C while the Pt/C has a higher CCE than the bimetallic catalyst at 1 M ethanol concentration. On the PtRh/C catalyst the highest CCE is measured at 5 M ethanol concentration followed by 10.9 M and 1 M.
7.3 Discussion and Conclusions

The EOR on carbon supported Pt and PtRh catalysts has been studied in chronoamperometric measurements at three different ethanol concentrations, 1 M, 5 M, and 10.9 M at 150 °C. It has been found that in general the best performance is achieved at an ethanol concentration around 5 M.

On the PtRh/C catalyst the ethanol concentration has a strong influence on the performance, with the highest and most stable performance at a 5 M concentration. On the Pt/C catalyst a similar performance is achieved at all ethanol concentrations up to a potential of 0.6 V. At the highest measured potential of 0.8 V the highest performance is achieved using 10.9 M ethanol, though the performance at 5 M concentration is comparable and appears to be more stable over time.

Both catalysts show a negligible activity at 0.2 V, and a low but steady performance at 0.4 V. The addition of Rh to Pt/C catalyst is not always advantageous, but leads to an increase in performance at high potentials and low ethanol concentration.

At the highest measured potentials of 0.6 and 0.8 V an increased activity can be observed on PtRh/C compared to Pt/C at 1 and 5 M ethanol concentration. Using 1 M ethanol and a potential of 0.8 V (and to a lesser degree 0.6 V) the current is unstable. This could be due to high oxide coverage of the catalyst surface or depletion of ethanol at the anode.

At the highest ethanol concentration of 10.9 M the integrated charges of the ion currents for \( m/z = 22 \) and 44 indicate the formation of acetaldehyde. The discrepancy between the charges for the two mass to charge ratios is bigger on PtRh/C than on Pt/C and occurs at lower potentials. Apparently under conditions where the ethanol to water ratio is shifted towards the ethanol the negative effect of less available Pt adsorption sites outweigh the positive effect of oxide donation from the Rh.

Like the formation of acetaldehyde, the formation of ethyl acetate is strongly influenced by the ethanol concentration, with a low ethyl acetate formation at 1 M ethanol concentration and formation of significant amounts at 10.9 M. Again the formation of the side product observed on the PtRh/C catalyst is higher than that on the Pt/C catalyst, especially at high potentials. When comparing the formation of ethyl acetate at different concentrations it has to be kept in mind that
the higher ethanol concentration probably leads to an increase in the formation ethyl acetate instead of acetic acid. Since the acetic acid is not detected, it is possible that the total amount of acetic acid and ethyl acetate produced is not as strongly influenced by the ethanol concentration.

There is a contradiction between the higher amount of side products detected and the higher CO$_2$ efficiency calculated for the PtRh/C catalyst with 10.9 M ethanol compared to those for the Pt/C catalyst with the same ethanol concentration. The CO$_2$ efficiency might be the less reliable observation due to its high error that has been discussed in Chapter 3.
8 Discussion, conclusions and perspectives

In the work described in this thesis, a novel experimental half-cell set-up was designed to study the ethanol oxidation reaction at elevated temperatures in the range of 120 to 180 °C. It offers the possibility to simulate the conditions in HT-PEM DEFCs on gas diffusion electrodes, especially the effect of the evaporated gaseous ethanol at temperatures above the boiling point of water, while most literature references measure the oxidation of more dilute solutions of ethanol in aqueous H₂SO₄ electrolyte. In contrast, using high ethanol molarities of several mol per liter in the feed gas proved advantageous in the presented set-up, because the more direct connection to the MS with the capillary (compared to a membrane inlet) allows water from the feed gas to enter the MS along with the organic substances and thus a high water content in the fuel feed has a negative impact on the mass spectrometric detection. The resulting experimental conditions are closer to those obtained in a HT-PEM DEFC single cell [81] than those obtained with pressurized liquid phase test cells [62,64,79,80], and can be conducted with comparatively small amounts of catalyst, membrane and GDL material.

This experimental set-up allows the product distribution in the exhaust gas to be measured by online mass spectrometry. Conditions that promote the complete oxidation of ethanol to CO₂ are known from literature studies of the oxidation of ethanol dissolved in liquid electrolyte at temperatures up to 100 °C. These general trends could be confirmed for the gas phase EOR in the temperature range from 120 - 180 °C.

The efficiency of CO₂ formation increases with:

- increasing temperature [64,81,161]
- the use of carbon supported Pt catalyst compared to Pt black [81]
- decrease of ethanol concentration [60,64,72,81]
- choice of a low electrode potential [64]

The effect of the temperature has been shown up to 160 °C. Beyond this temperature the catalyst has been found to show signs of degradation due to carbon corrosion, which leads to a lowered performance. While the thermal activation of the C-C bond breaking has a strong influence on the
CO₂ efficiency, the other operation conditions can have a significant impact and have to be optimized as well to achieve high CO₂ efficiencies.

Using a carbon supported catalyst instead of an unsupported catalyst has the advantage of providing a larger active surface area at a reduced metal loading. In addition it suppresses the formation of acetaldehyde, because a thicker catalyst layer with a highly dispersed catalyst increases the retention time of the ethanol close to the catalytic surface. This leads to a higher probability of the acetaldehyde formed in a previous oxidation step to readсорb and be oxidized further to CO₂ or acetic acid or ethyl acetate [81].

The ethanol concentration has been found to have a significant influence not only on the product distribution but also on the potential dependence of the Faradaic current. Using high molarities of several mol per liter ethanol, it has been found that the oxidation wave, that can usually be observed in the ethanol oxidation current during a CV scan around 0.8 V, is shifted to significantly higher potentials. Because the oxidation wave is caused by a decrease of catalyst activity due to blockage with adsorbed oxide species [64], it is hypothesized that at high concentration ethanol and water in the gas phase compete strongly for free electroactive catalyst sites. This leads to a shift of the onset potential for the adsorption of water and subsequent oxide formation on the catalyst surface to a higher potential.

The effect leads to a near linear increase of the Faradaic current in an anodic CV scan, and a similar decrease in the cathodic scan if the upper vertex potential chosen is lower than the maximum of the oxidation wave. Approximately linear current over potential curves have been reported up to potentials of 0.8 V [160,118,119], 0.9 V [166] or even 1.0 V [63]. Rao et al. [81,82] measured CV curves similar to the one presented in Chapter 5 with a Nafion® [81] and AEM [82] fuel cell set-up operated in half cell mode. In the case of the Nafion® fuel cell, the near linear CV curve could only be observed at 1 M ethanol concentration, while a 0.1 M ethanol concentration leads to a CV with an oxidation wave with a maximum around 0.8 V. A near linear CV curve has also been reported on sputter deposited Pt in 0.1 M ethanol and 0.1 M KOH electrolyte up to a potential of 1.1 V [57].

In addition to the choice of reaction conditions, the addition of Rh to the Pt electrocatalyst has been studied. Previous results by Bach Delpeuch et al. confirmed that the addition of Rh promotes the complete oxidation of ethanol at room temperature in dilute H₂SO₄ [123,125]
However, in the present study the effects of the Rh on the product distribution are not conclusive and a positive effect on the overall performance has been found mainly at potentials above 0.4 V. It is possible that the Rh is made inert by adsorption of phosphate as has been shown to happen for Ru in a phosphoric acid based DMFC \[^{30}\].

It would be interesting if the effect of the phosphate adsorption could be isolated in some way from the effect of the high temperature and the reaction in the gas phase instead of the liquid phase. This could be possible either by using PBI doped with other strong acids like sulfuric acid at high temperature \[^{135}\], or by a study comparing the EOR in dilute phosphoric acid to that in dilute sulfuric acid at low temperature.

The set-up was developed and employed during this work for the study of the ethanol oxidation reaction (EOR) on supported and unsupported Pt electrocatalysts in an phosphoric acid-doped PBI-based system in the high temperature range. In that sense, the activity and selectivity of other add metals to the electrocatalyst for the EOR under HT-PEMFC conditions would be one perspective for further study. For example tin (Sn) and ruthenium (Ru), but also tungsten (W), palladium (Pd), rhenium (Re), molybdenum (Mo), titanium (Ti) and cerium (Ce) have all been investigated before as binary or tertiary add metals to Pt/C for the EOR and have shown some promise \[^{93}\].

But there are other possible applications of the set-up. Aside from the studies on the EOR, it has already been used as well in a high temperature H3PO4/PBI-based system to study the activity of various catalysts for the oxidation of H2S, which is a possible contaminant in hydrogen and which poisons Pt catalysts, to SO2 \[^{167}\].

In principle, the set-up could be used for testing numerous anodic or cathodic systems with gaseous reactants. For example the oxidation of other HT-PEMFC fuels, like hydrogen, methanol or dimethyl ether (DME), at the anode side of a DAFC could be studied.

The set-up would also be well suited for studies on the carbon corrosion of different materials of gas diffusion layer and catalyst support under HT-PEMFC conditions. The set-up has been built especially for high temperature applications. However, as long as the membrane and educts used allow for it, measurements at temperatures lower than 120 °C might be possible. This offers the
possibility to carry out mass spectrometric studies on half-cell reactions using membrane and electrode materials as they could be used for MEA preparation.

The limit of the set-up concerning comparison with a working fuel cell is, on the one hand, its lack of a comparable flow field, which will influence water management. On the other hand, the behavior of the PBI membrane in contact with the concentrated phosphoric acid might not be comparable to the same membrane in an actual fuel cell, where a limited amount of phosphoric acid is available and may be washed out during operation.

In conclusion the work described in this thesis offers new insight into the EOR under HT-PEMFC conditions. It has been found that the positive effect of an increased temperature that has been predicted based on measurements with ethanol dissolved in aqueous sulfuric acid electrolyte might be curbed by the negative effects of phosphate adsorption from the concentrated phosphoric acid electrolyte on the activity and selectivity of the catalyst. Nonetheless high efficiencies for the CO$_2$ formation could be reached at 150 °C by choosing a medium ethanol concentration of 5 M, a carbon supported catalyst and a low potential around 0.4 V. The addition of Rh to the Pt/C catalyst shows some promise, but the Rh might suffer from the adsorption of phosphate to the catalytic surface even more than the Pt. In addition it could be shown that commercial HT-PEMFC materials like GDLs and carbon support show detectable carbon corrosion under HT-PEMFC working conditions.
9 Literature references


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