Reformate Hydrogen Fuel in PEM fuel cells: the Effect of Alkene Impurities on Anode Activity

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Reformate fuel cells can function as bridging stones from fossil to hydrogen fuel. They can, for instance, be used in APUs in diesel vehicles or in microCHP operated on natural or biogas. Instead of needing a hydrogen infrastructure, fossil or biofuel is reformed on-board or on-site, resulting in a mixture of hydrogen, CO_2, nitrogen, water vapor and traces of CO, sulfur species and hydrocarbons. While CO and sulfur species are well known poisons [1] for the anode of a PEM fuel cell and CO_2, although less poisonous, is known as a potential source of CO [2], the effect of hydrocarbon traces has not been studied as much.

Previous studies by our group indicate that although the effect of ethene in a fuel cell is small [3], toluene is a potential fuel cell poison [4]. Studies in acidic electrolyte [5] indicate that chain length has a considerable effect on the adsorption and oxidation of hydrocarbons on Pt catalyst. In this study we will discuss the adsorption and desorption behavior of alkenes on the anode catalyst of a PEM fuel cell in light of new results on propene.

The results show that the adsorption and subsequent desorption by reduction and/or oxidation is highly dependent on the adsorption potential. This can be seen in Figure 1, which depicts the stripping curves after exposure at various potentials. Similar to ethene [3], propene appears to be adsorbed mainly at catalytic sites that are not occupied by hydrogen. This can be concluded from the limited adsorption at potentials within the hydrogen region and the subsequent increase in the oxidation peak size as the adsorption potential increases towards the upper limit of the region, after which is starts to decrease again as the adsorption potential increases into the oxidation range.
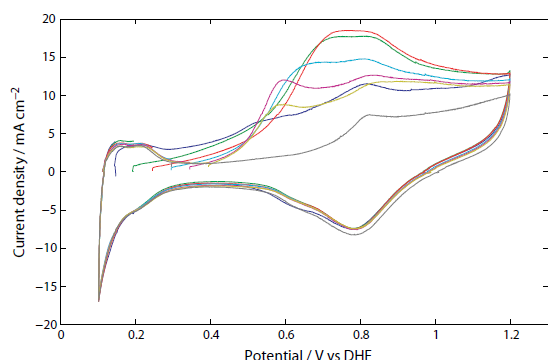

Figure 1: Stripping cyclic voltammetry of propene on Pt/C in a fuel cell after exposure at various adsorption potentials.

The oxidation of propene ad-species takes place in more than one step and the shape of the oxidation peak is very dependent on adsorption potential. Fairly high potentials are needed to oxidize propene to CO_2, and, similar to toluene [4], multiple sweeps are needed to recover the electrode surface, even at 80°C and 90% RH. In contrast, all ethene species are removed in a first oxidative sweep

to 1.2 V vs DHE at the same conditions. As seen in Figure 2 the oxidation peaks correspond well with the mass spectrometry signal m/z 44, which is normally attributed to CO_2.

A significant amount of propene ad-species can be removed in a reductive sweep prior to the oxidative sweep. This causes changes to the shape subsequent oxidation peaks, similar to those induced by altering the adsorption potential. This can be seen in Figure 2 (top). Ethene ad-species are also partly reductively desorbable [3], but the amount is significantly smaller than in the case of propene. Even toluene ad-species are reductively desorbable to a small extent [4].
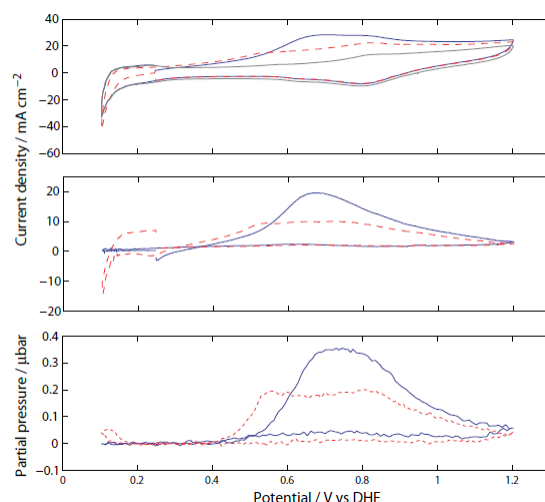

Figure 2: Stripping cyclic voltammetry of propene adsorbed at 0.25 V vs DHE (top), base curve (gray), positive stripping (blue) and negative stripping (red dashed). Also shown are stripping curves with the baseline subtracted (middle) and the accompanying mass spectrometric signal for m/z = 44 (bottom).

Although propene was found to be more easily reduced (to propane) at low potentials than ethene (to ethane), the presence of hydrogen during the adsorption appeared to have a larger effect on the adsorption of ethene than on propene. The oxidation peak of ad-species formed from ethene was almost negligible when hydrogen was present during adsorption, while, although smaller, the peak was clearly visible for propene ad-species.

Overall, the results of this study indicate that propene is a stronger poison to the anode catalyst than ethene, but perhaps not as strong at toluene.

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