Ethanol oxidation studied by operando XAFS

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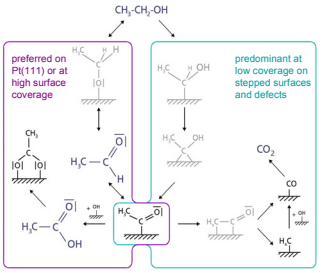
Introduction

The use of liquid alcohols as anode fuel is anticipated to make fuel cells competitive with batteries in applications with long run-time and low power requirements. Direct ethanol fuel cells (DEFC), however, suffer from the complex oxidation reaction which is known to depend strongly on the catalyst structure.

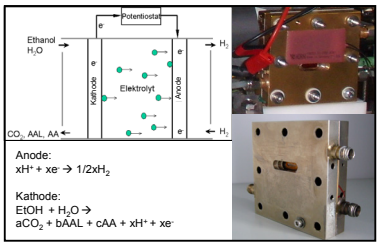
In order to better understand the correlation, XAFS measurement were performed on commercial available catalyst in an operating fuel cell. EXAFS was used to obtain the structural information, whereas the Δμ-XANES method was used to get insights into number and kind of adsorbates on the catalyst surface.

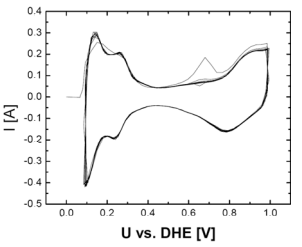


Summary of the ethanol electrooxidation on Pt/C

Experimental

Measurements were performed at the XAS Beamline at ANKA, Karlsruhe, Germany. The measurements were carried out in transmission mode during half cell measurements at different potentials and atmospheres for a Pt/C, PtRu/C and PtSn/C catalyst. Spectra in an energy range between 11314 and 12564eV were taken for hydrogen, water, ethanol 1M and methanol 1M under certain potentials measured vs. DHE.





Right side:schematic illustration of half cell measurement carried out in a fuel cell (photographs) Left side: Cyclic voltammogram of Pt/C in water measured in half cell mode

Data analysis

Δμ-XANES The absorption coefficient μ was obtained from the raw data with the ATHENA code. The Δμ were obtained by subtracting the measurement for water at 0.45 V vs. DHE from the appropriate spectra at a certain condition x.

$$\Delta\mu(x)_{H_2O,0.45V} = \mu(x) - \mu(clean, 0.45V)$$

The relative amount of OH on the surface is determined by substraction the portions of hydrogen or C-species signature the $\Delta\mu(x)_{H2O,\ 0.45V}$.

$$\Delta\mu(O(H),x)_{H_2O,0.45V} = \Delta\mu(x)_{H_2O,0.45V} - a \cdot \Delta\mu(C-species, 0.3V)_{H_2O,0.45V}$$

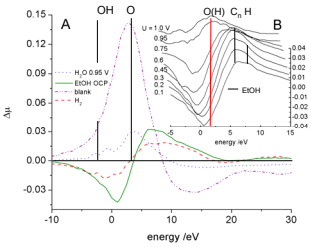
In the case of Pt/C the representive C-species is found at 0.3 V vs DHE in ethanol and 0.45 V in methanol. The C-species contribution for PtRu and PtSn can be calculated out by using the measurement with ethanol at 0.1 V vs. DHE respective the measurement in hydrogen atmosphere.

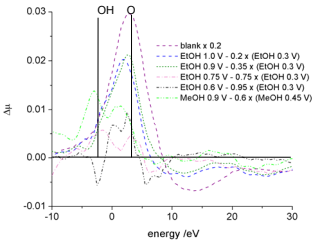
$$\Delta\mu(O(H),x)_{H_2O,0.45V} = \Delta\mu(x)_{H_2O,0.45V} - a \cdot \Delta\mu(EtOH, 0.1V)_{H_2O,0.45V}$$

$$\Delta\mu(O(H),x)_{H_2O,0.45V} = \Delta\mu(x)_{H_2O,0.45V} - a \cdot \Delta\mu(H_2)_{H_2O,0.45V}$$

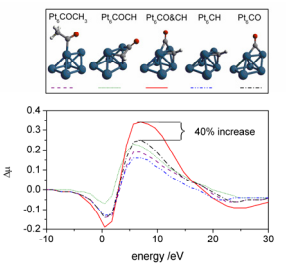
Δμ-XANES for the Pt/C catalyst

Difference spectra

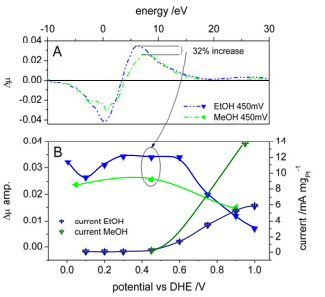




Δμ Simulations
using FEFF



Current and Δμ amplitude
vs. potential for ethanol and methanol

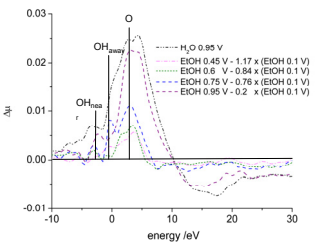


- C-C bond is splitted at 0.45 V, less OH in atop position during EOR

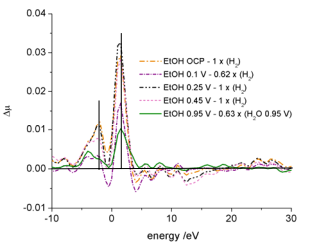
Δμ-XANES for PtRu/C and PtSn/C catalyst

Difference spectra Δμ(O(H), x)

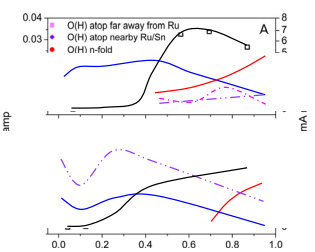
PtRu/C



PtSn/C



Current and Δμ amplitude
for ethanol for PtRu (A) and PtSn (B)



PtSn
- heavily oxidized at all potentials
- significantly lower Δμ for C-species

PtRu
- oxidation depends strongly on potential
- reaction starts with O(H) adsorption
- current maximises with OH_{away}

Conclusions

X-ray absorption spectroscopy was used to gain a better understanding of the processes leading to the incomplete oxidation of ethanol.

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