A case for core-shell catalysts in fuel cells and water electrolysis

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Low- to medium temperature fuel cells operating with organic fuels, such as the direct methanol fuel cell (DMFC), are currently limited by the unavailability of catalytically efficient and stable catalysts. The superior activity of the Pt-Ru alloy system as compared to Pt and Ru mono-metallic catalysts for oxidizing CO and small organic molecules such as methanol is frequently explained by a conceptual splitting of the effects of alloying into a bifunctional mechanism[1] and a ligand effect.[2] Other architectures than alloys, such as core-shell structures[3,4] may change the catalytic activity and stability significantly for a given composition both compared to the single metals and to the alloy. Recent results thus indicate that trapping of the Ru inside a shell of the more stable Pt may retain a significant fraction of the electrocatlytic activity for oxidation of pre-adsorbed CO (CO-stripping) associated with the alloy without dissolution of Ru[4] associated with alloys.

Fuelling hydrogen fuel cells in renewable energy context primarily rely on water electrolysis. However, also for fuelling DMFC's in a methanol cycle may there be a need for hydrogen. Frequently, anode oxide catalysts containing two different metals are also employed in water electrolysis, usually intended to be solid solutions. Also for these there are reports about metal-metal interaction, although within a less developed theoretical framework.

In this contribution we present and discuss the activity and stability of bimetallic catalysts for oxidation of small organic molecules in fuel cells and for water electrolysis. We will compare metal-metal interaction in both systems, and discuss the application of core-shell structured catalysts in both technologies.

Experimental
Ru@Pt catalysts on Vulcan XC-72 were synthesized and characterized as described in Ref. 3 and 4. $Ir_{1-x}Ru_xO_2$ was synthesized characterized as in Ref. 5. In addition a similar series iridium-ruthenium oxide catalysts were synthesized by a sol-gel technique.

Results and discussion
Results of characterization of the Ru@Pt/C catalysts by cyclic voltammetry, transmission electron microscopy (TEM), X-ray diffraction, and EXAFS analysis indicated that the surface of the catalysts contained no ruthenium. A significant negative displacement of the CO stripping peak-potential as compared to Pt was among the chief indications of Pt being deposited on the Ru cores. Typical particle sizes were around 4 nm.

Heat-treatment of the Ru@Pt catalysts led to significant changes in the structure, as expressed in a shorter Pt-Pt bond length and a more significant extent of alloying as

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calculated from coordination numbers (by EXAFS), as displayed in Fig. 1. Included in Fig. 1 are the peak potential in CO-stripping and the activity for methanol oxidation in chronoamperometric experiments as a function of the heat-treatment temperature.
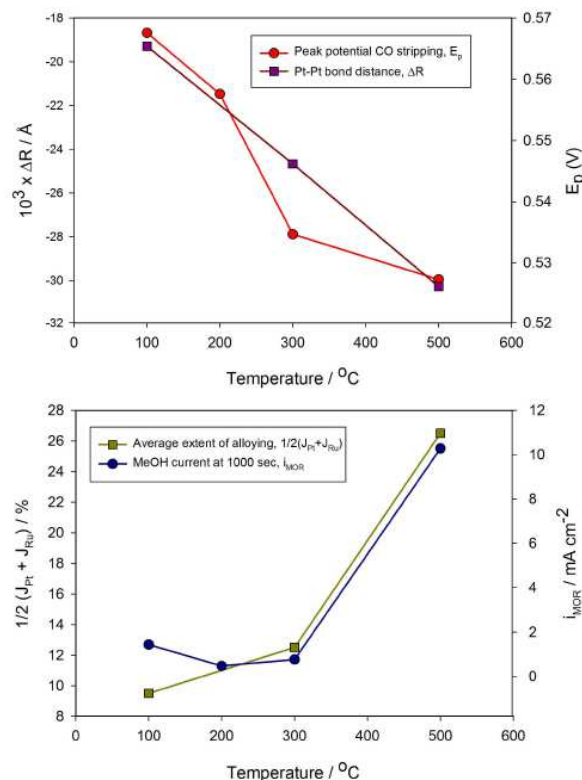

Figure 1. Peak potential in CO stripping and bond length (top) and methanol oxidation current and extent of alloying (bottom) as a function of heat-treatment temperature for a Ru@Pt catalysts on Vulcan XC-72.

As can be seen from the figure the CO-stripping potential correlates well with the Pt-Pt bond length as expected[2], but less with the extent of alloying. For the methanol-oxidation current the correlations are reverse.

For the water-electrolysis catalysts ($Ir_{1-x}Ru_xO_2$) a series of comparisons between solid solutions and physical mixtures gave the same catalytic activity independent of the nature of the mixture, i. e. whether atomic or physical. In contrast with previously published results for $Ir_{1-x}Ru_xO_2$, these results therefore indicate the absence of any metal-metal interaction of the type displayed in the bimetallic catalysts discussed above. However, whereas the architecture of the bimetallic catalysts may be used to improve activity, an architecture resembling the core-shell structure may be used to reduce the amount of precious metal for the water-electrolysis catalyst without loss of activity in the latter case.

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