

Palladium-based bimetallic catalysts for Alkaline Direct Alcohol Fuel Cell (ADAFc)

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Direct Alcohol Fuel Cells (DAFCs) have attracted enormous attention as potential power sources for electronic devices and transportation due to higher energy density than gaseous fuels such as hydrogen. But the slow electrode-kinetics of the alcohol oxidation is hindering the commercialization of DAFCs. Recent studies show that the electrocatalytic activity for alcohol oxidation in alkaline media is much higher than that in acidic media. The oxidation of methanol (MeOH) and ethanol (EtOH) in alkaline media has shown higher current densities and smaller overpotentials compared to those in acidic media.[1-3] Besides this the catalyst materials used for ethanol oxidation and oxygen reduction in Alkaline Direct Alcohol Fuel Cells (ADAFcs) are cheaper and more efficient than Pt.[4]

Pd has proved to be a good electrocatalyst for alcohol oxidation in alkaline medium, showing higher activity and better steady-state behavior than Pt.[5,6] To improve the activity and stability towards alcohol oxidation, Pd-based catalysts including Pd-oxide composite, Pd-based binary and Pd-based ternary catalysts have been investigated by several research groups.

In this work carbon supported bimetallic Pd-Ni and Pd-Ag catalysts were prepared and evaluated electrochemically for methanol and ethanol oxidation in alkaline media. Interesting alcohol electrooxidation results were obtained and compared to that of Pd/C electrocatalyst.

Electrocatalysts were prepared by reduction of the metal salts with sodium borohydride in aqueous sodium citrate and carbon black suspensions. Thus electrocatalysts with a loading of 20 wt% metal on carbon support were received. Thereby the ratio of Pd to Ag and Pd to Ni was varied, respectively, as summarized in Table 1. The actual loading of catalyst on carbon support was measured via thermogravimetric analysis (TGA) in air in the range of 30 to 700 °C at 10° min⁻¹.

Table 1: Summary of obtained electrocatalysts. Loading on carbon was measured by TGA.

Catalyst	Ratio Pd: Metal	Calculated loading [wt%]	Measured loading [wt%]
Pd/C		20,0	21,0
Pd ₃ Ni ₁ /C	5:1	20,0	20,0
Pd ₃ Ni ₁ /C	3:1	20,0	19,6
Pd ₃ Ag ₁ /C	5:1	20,0	20,7
Pd ₃ Ag ₁ /C	3:1	20,0	20,3

For electrochemical measurements a catalyst ink was prepared with polytetrafluoroethylene (PTFE) as binder and ethanol as solvent. Catalyst ink was pipetted onto a polished glassy carbon electrode (GCE) and air dried to get a thin film electrode.

Cyclic voltammetry (CV) and chronoamperometry (CA) were conducted using a standard three-electrode cell. The modified GCE, a Pt foil electrode and a Hg/HgO electrode (MMO) served as the working electrode, the counter electrode and the reference electrode, respectively. Electrochemical experiments were carried out in Ar-purged 1M KOH + 1M alcohol (ethanol or methanol) solutions.

CV and CA results showed similar rankings of the

electrocatalytic activity of the prepared catalysts for alcohol oxidation reaction. CA curves are shown in Figure 1 and 2 for MeOH and EtOH oxidation, respectively. The initial high currents were due to the double layer charging and possibly the oxidation of some adsorbates. A gradual decrease in the mass activity with time is observed indicating the poisoning of the catalyst. For MeOH electrooxidation Pd₃Ag₁/C and Pd₃Ni₁/C catalysts show higher mass current densities than Pd/C, which indicates a more efficient electrocatalytic behavior. Besides this Pd₃Ni₁/C shows a lower poisoning rate than Pd₃Ag₁/C. For the EtOH electrooxidation Pd₃Ag₁/C and Pd₅Ag₁/C catalysts are much more efficient than Pd/C.

Further work will include differential electrochemical mass spectrometry (DEMS) to identify product distributions for alcohol oxidation reactions in alkaline media for these electrocatalysts.

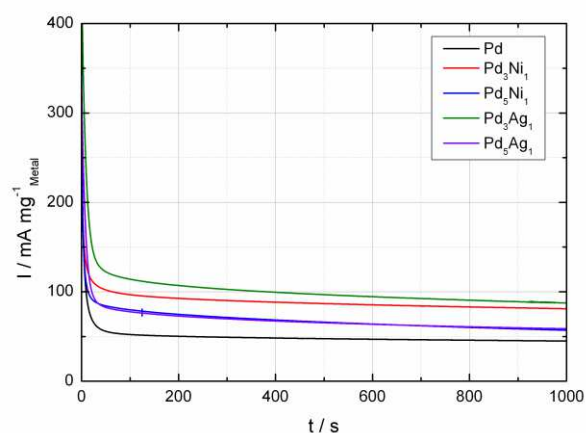


Fig. 1 – Chronoamperometric curves at -0.25 V vs. MMO of methanol electrooxidation in 1M KOH + 1M MeOH on Pd/C, Pd₃Ni₁/C, Pd₃Ni₁/C, Pd₃Ag₁/C, Pd₅Ag₁/C at room temperature.

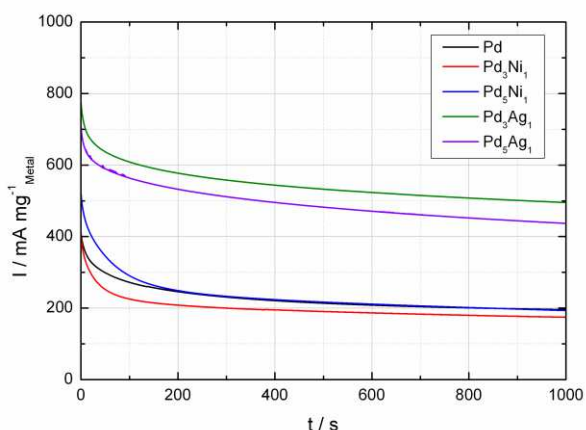


Fig. 2 – Chronoamperometric curves at -0.25 V vs. MMO of ethanol electrooxidation in 1M KOH + 1M EtOH on Pd/C, Pd₃Ni₁/C, Pd₃Ni₁/C, Pd₃Ag₁/C, Pd₅Ag₁/C at room temperature.

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