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Pd-Au DEPOSITES ON NI-FOAM AS ANODIC ELECTROCATALYSTS FOR DIRECT BOROHYDRIDE FUEL CELL

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Abstract. In this study, Pd and Au were deposited on Ni-foam and examined as electrocatalysts for borohydride electrooxidation. The Pd-Au deposits were developed by co-deposition from mixed solutions of Pd^{2+} and Au^{3+} with different ratios of both metals. The corrosion resistance of the obtained materials in 6M KOH electrolyte was evaluated by linear voltammetry. The electrocatalytic performance of the developed electrodes towards borohydride electrooxidation reaction was analysed by means of chronopotentiometric and anodic polarization measurements in stabilized alkaline solution of sodium borohydride. The obtained results with different electrodes were compared and discussed in respect to their potential application as anodes in Direct Borohydride Fuel Cells.

Keywords: Pd-Au catalyst, borohydride electrooxidation, direct borohydride fuel cell

Introduction

The issue of renewable energy is becoming significant due to increasing power demand, instability of the rising oil prices and environmental problems. Among the various renewable energy sources, fuel cells are gaining more popularity due to their higher efficiency, cleanliness and cost-effective supply of power demanded by the consumers (Kirubakaran et al., 2009). Among the different types of fuel cells, direct borohydride fuel cells (DBFC) have attracted increasing interest over the past decade, because of their favorable reaction kinetics in alkaline media, higher energy densities achievable and the easy handling of the liquid fuels (Ma et al., 2009; Ponce de Leon et al., 2006). DBFC are devices that convert chemical energy stored in borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. Usually, a DBFC employs an alkaline solution of sodium borohydride ($NaBH_4$) as a fuel and oxygen or hydrogen peroxide as an oxidant. DBFC has some attractive features such as high open

circuit potential, easy electrooxidation of BH_4^- on non-precious metals such as nickel, low operational temperature and high power density. Despite the high energy densities available during the oxidation of BH_4^- , not all of the potential chemical energy stored in BH_4^- converts into electricity. A hydrolysis process of the borohydride is observed with generation of hydrogen gas and formation of overpotential. So, further developments of catalysts, membrane materials and fuel cell systems are essential. Hydrogen evolution during the DBFC operation can be suppressed by using a composite catalyst or a hydrogen storage alloy as the anode catalyst via a quasi 8-electron reaction, using metals with high hydrogen overpotential, such as Au and Ag as the anode catalyst via an intrinsic 8-electron reaction or modifying and optimizing fuel composition, adding hydrolysis inhibitors (Liu & Li, 2009; Gyenge, 2004). It is well known that Pt and Pt-alloys (Pt-Au, Pt-Ni, and Pt-Ir) and lower cost Pd, Au and Ag metals perform high electrocatalytic activity with respect to borohydride oxidation reaction (Gyenge et al., 2006).

Motivated by the idea that a monometal catalyst can be stabilized with the incorporation of gold (Au) due to its unique electron-withdrawing effect to neighboring primary metal atoms, in this work we produced Pd–Au deposits on Ni-foam and explored them as electrocatalysts for the BH_4^- oxidation reaction in an alkaline medium.

Experimental

Three types of Pd-Au materials were prepared using Ni-foam as a support. The Pd-Au deposites were developed by co-deposition from mixed solutions of Pd^{2+} and Au^{3+} with different ratios of both metals. The stock solutions were 2 % $PdCl_2$ in 0.1 M HCl and 2% $HAuCl_4$ in 0.1M HCl. Relative compositions between Au and Pd at the particle surfaces as well as in bulk phases could be modulated by controlling the molar ratios between metal precursors in the feeding solutions (Lee et al., 2010; Nagaiah et al., 2013). Three mixtures (bulk phase) from the described above solutions in ratio 50:50, 70:30 and 90:10 (wt./wt.) were prepared. A pieces of Ni-foam (RACEMAT, RCM-Ni-2733.03, pore diameter d=0.6mm, SSA=2500m^2/m^3) with geometric area of 1 cm^2 was immersed in the prepared solution for 10 seconds. The samples prepared from the initial solutions in ratio 50:50 are marked as Pd:Au=50:50, respectively Pd:Au=70:30 and Pd:Au=90:10 (Table 1).

The structural details and the particle sizes of the prepared catalysts were characterized by SEM investigation.

The corrosion behavior of the prepared materials in 6M KOH electrolyte was explored by means of linear voltammetry. The experiments were performed in three electrode cell by using potentiostat-galvanostat PJT 35-2 (RADIOMETER-TACUSSEL, France)

Table 1. Bulk phase composition of solutions for preparation of Pd:Au catalysts

Material	Bulk phase composition ratio (wt:wt)			Molar composition ratio of the bulk phase (mol:mol)		
	$2\%PdCl_2$	:	$2\%HAuCl_4$	Pd^{2+}	:	Au^{3+}
Pd:Au=50:50	50	:	50	2	:	1
Pd:Au=70:30	70	:	30	5	:	1
Pd:Au=90:10	90	:	10	20	:	1

with electrochemical interface IMT-101 and Volta Master 2 software for data processing and acquisition. The examined material was connected as a working electrode, Hg/HgO was used as a reference electrode and Pt as a counter electrode. The potential was swept from -500 mV to -100 mV with 5 mV/s scan rate. The obtained voltammograms were plotted in coordinates log *i* vs. *E* for evaluating the corrosion potential and rate. The coordinates of the cross point of the extrapolated linear regions of the anodic and the cathodic part of the curves correspond to the corrosion potential and the corrosion current.

The catalytic activity of the prepared catalysts towards borohydride electrooxidation was examined by polarization measurements in 1.3M $NaBH_4$/6M KOH electrolyte, using the upper described three-electrode arrangement. Polarization curves were obtained increasing stepwise the anodic current from 0 to 1500 mA. The duration of each galvanostatic step was 30 s and the achieved electrode potential was recorded by the potentiostat-galvanostat. For each pair current-potential the power was estimated using equation $P = E.I$ and the corresponding power curves were also plotted.

Galvanostatic discharge in 1.3M $NaBH_4$/6M KOH at applied anodic current 50 mA was also carried out with the explored catalysts. The discharged capacity of each material was calculated from the obtained chronopotentiograms.

The described experiments were performed with as-prepared (untreated) samples as well as with samples pretreated by immersion in 1.3M $NaBH_4$/6M KOH for 24 hours.

Results and discussion

SEM image of the supported Pd:Au=50:50 material is shown on Fig. 1. Dense coverage of different-sized dendritic particles is formed on the support surface, which is probably a result of the formation of numerous metallic nuclei followed by subsequent fast growth of particles.

Corrosion curves, obtained with the examined catalysts in strong alkaline electrolyte, are presented in Fig. 2. More negative corrosion potentials and higher corrosion

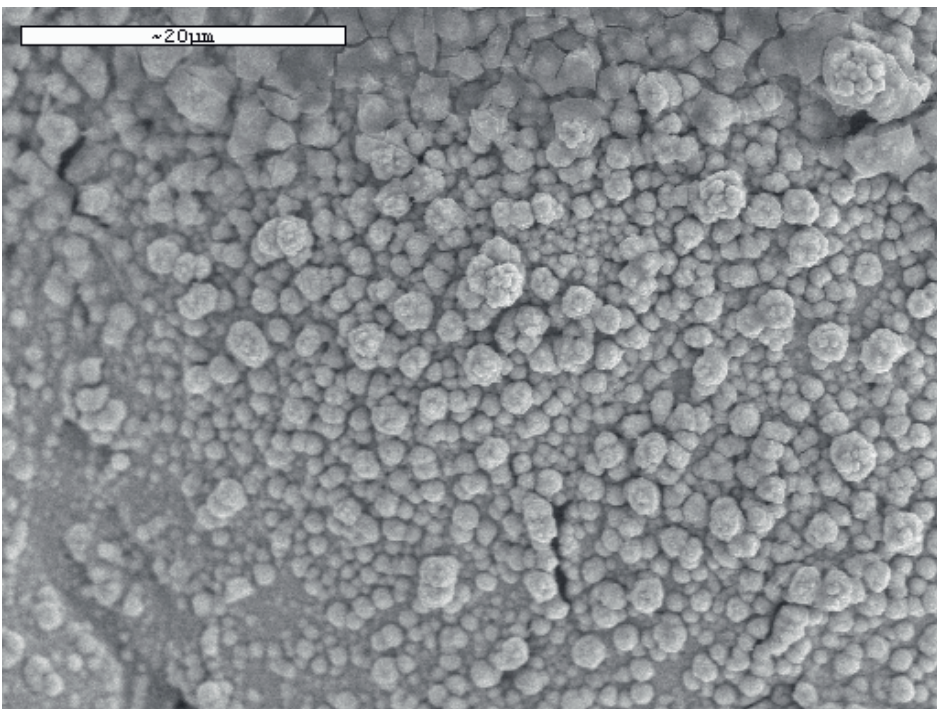

Fig. 1. SEM image of Pd:Au=50:50 material

rates are observed for all co-deposited materials compare to those for the bare support, which indicates that the Ni-foam posseses higher corrosion resistance than the produced supported catalysts. The lower corrosion resistance of the bi-metallic catalysts could be assigned to their compositional and structural inhomogeneity, resulting in development of numerous microgalvanic cells on the electrode/electrolyte interface. Such assumption is supported by the fact that the catalyst, produced from electrolyte containing the least amount of second metal (Pd:Au=90:10), possesses the highest corrosion resistance among explored co-deposits.

Polarization and power curves, obtained with examined materials in borohydride-containing electrolyte, are shown in Fig. 3. The maximum power values, achieved with all Pd:Au supported catalysts, are with an order of magnitude higher than that obtained with the Ni-foam, which reveals the high potential of the co-deposited Pd-Au electrocatalysts as anodes in DBFCs. The comparison of the results of the treated and untreated samples shows that the treatment of the samples increases the performance of

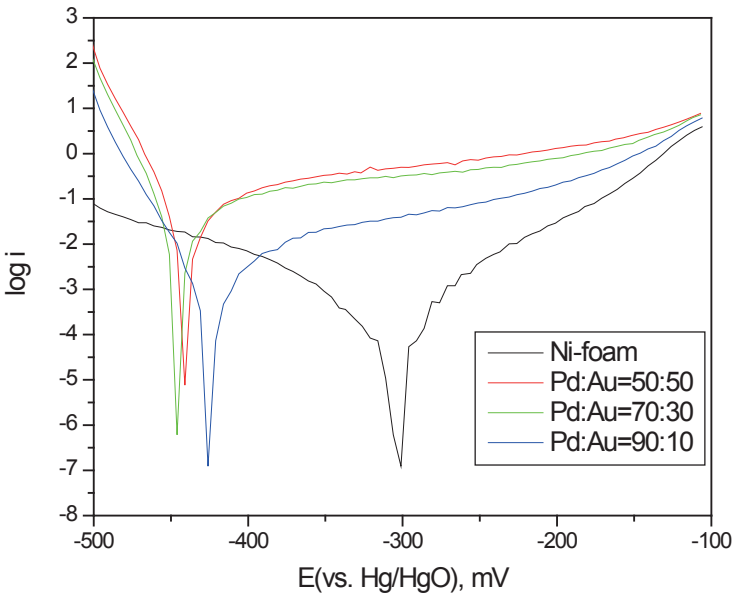

Fig. 2. Linear voltammograms of the examined materials in 6M KOH

the catalysts with about 50 % (Table 2). Additional experiments on the mechanism of the reactions are needed to explain exactly the reason of the observed activation.

Table 2. The electrochemical characteristic of the examined materials

Material	Materials, untreated		Materials, treated in 1.3M $NaBH_4$/6M KOH		Discharged capacity
	I, mA	P, mW	I, mA	P, mW	Q, mAh
Pd:Au=50:50	460	224	1050	522	900
Pd:Au=70:30	640	332	1100	543	975
Pd:Au=90:10	640	263	960	447	1100

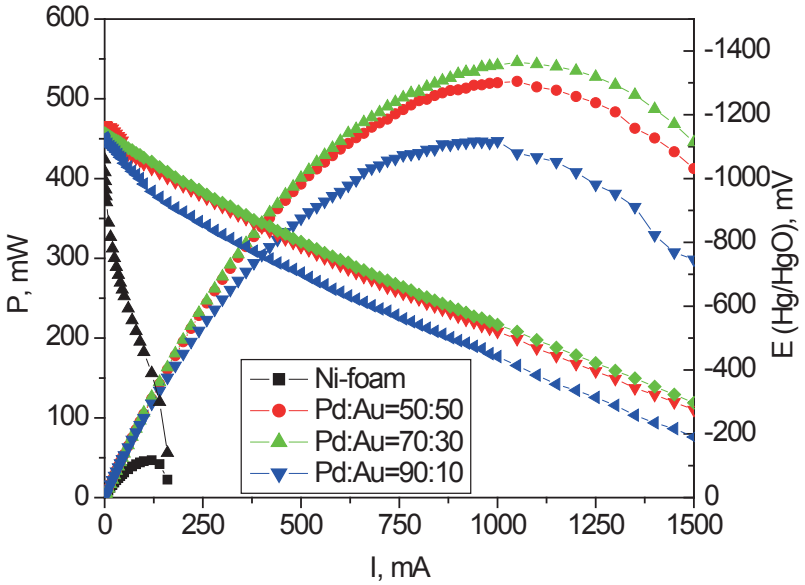

Fig. 3. Polarization and power curves obtained with the examined materials in 1.3M $NaBH_4$/6M KOH

The discharged curves, shown in Fig. 4, confirm the high discharged capacity of the examined catalysts in stabilized borohydride-containing electrolytes. The discharged capacity of Pd:Au = 90:10 reached up to 1100 mAh or 730 mAh/g $NaBH_4$. The high capacity of the examined deposits could be explained with the high catalytic activity of the Pd towards borohydride electrooxidation and the co-deposition of Au suspends the borohydride hydrolysis.

Conclusion

Three types of Pd:Au particles on nickel foam were developed and investigated. Compared to the nickel foam, the Pd-Au-modified catalysts exhibit increased catalytic activity for borohydride electrooxidation reaction. Taking into account the easy sample preparation and the performed activity and stability, it turns out that the Pd-Au deposits on Ni-foam exhibit an enhanced catalytic activity and could be used as potential anodes in the DBFC.

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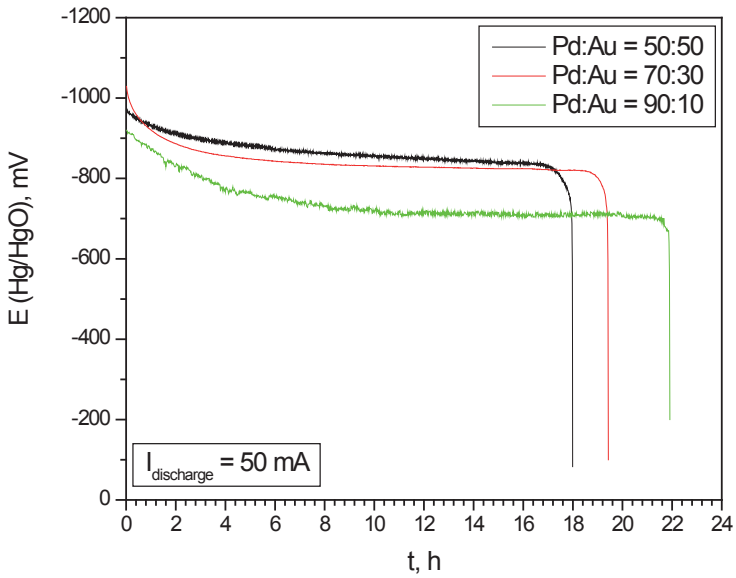

Fig. 4. Discharge curves obtained with the examined Pd:Au/Ni-foam electrodes in 1.3M $NaBH_4$/6M KOH

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