HYDROGEN ELECTROSORPTION IN PALLADIUM AND PALLADIUM-RHODIUM ALLOYS DEPOSITED ON RETICULATED VITREOUS CARBON (RVC)

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INTRODUCTION

Reticulated vitreous carbon (RVC) is an inexpensive and chemically inert carbon material characterized by an open pore structure and highly developed surface. It has been widely applied as an electrode material, including the use as a substrate for deposition of various metals, such as Au, Pd, Rh, Pt, Ir, Ni, Nb, and their alloys. Due to its unique properties, RVC is particularly suitable for studies on electrochemical systems and can be regarded as an electrochemical matrix for the electrochemical and electrochemical power issues.

Palladium and these alloys are intensively investigated as hydrogen sorption systems. The Pd-Rh system seems to be particularly interesting, since for a low Rh content the amount of absorbed hydrogen is equal to or greater than in pure Pd, it is an exception to the rule that Pd alloying with a non-absorbing element (such as Rh) reduces the hydrogen absorption capacity.

In this work we present the results of cyclic volumetric studies on hydrogen adsorption in Pd and Pd-Rh alloys deposited on RVC. This subject is connected with the possibility of future applications of RVC-based materials as hydrogen storage systems. The behavior of these materials as phase changing-discharging systems was investigated.

EXPERIMENTAL

Reticulated vitreous carbon (RVC) of 20 ppi porosity grade has been used as a matrix for electrodeposition of Pd and Pd-Rh alloys. The electrodes were in the form of blocks of a volume of 0.2-0.6 cm³ and an area of several cm². RVC substrate was always cleaned with acetone followed by keeping in boiling water for ca. 20 minutes. Additionally, RVC was electroplated with Au and an Au wire (99.9 %, 15 mm diameter) was also applied as substrate for the deposits. The deposition conditions that allowed us to obtain good deposits are summarized in Table 1.

The time of electrolysis was dependent on the desired thickness of the deposit, which was estimated from the charge passed and the substrate area. The thickness was in the range 0.6-1.0 microns in order to control the amount of absorbed hydrogen (limited volume electrodes). The morphology of the obtained surfaces was examined by a LEO 435VP scanning electron microscope (SEM). Bulk compositions of Pd-Rh alloys were in the range 92-97 % Pd, as determined in electrochemical experiment from the potential of a φ-phase transition, which was found to depend linearly on bulk Rh content.

All experiments were performed at room temperature in 0.5 M H₂SO₄ solution deoxygenated using an Ar stream. A three electrode cell was used with Hg/HgO/0.5 M H₂SO₄ as the reference electrode and a Pt plate as the auxiliary electrode. All potentials are referenced with respect to the SHE.

RESULTS AND DISCUSSION

Figs. 1 and 2 present SEM images of Pd and Pd-Rh alloys deposited on various substrates. (a) Au wire, (b) bare RVC, and (c) RVC electroplated with a thin Au layer (i.e. 1 μm). These photographs demonstrate that good deposits were obtained, tightly covering the matrix surface.

Table 1. Characteristics of Pd and Pd-Rh deposits on RVC substrate

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Specific Pseudocapacitance (F/g)</th>
<th>Electroactive Mass (F/g)</th>
<th>Total Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Au</td>
<td>3300-4000</td>
<td>7-11</td>
<td></td>
</tr>
<tr>
<td>Pd-Rh/RVC</td>
<td>1100-2200</td>
<td>250-540</td>
<td></td>
</tr>
<tr>
<td>Pd-Rh/Au/RVC</td>
<td>1500-2200</td>
<td>220-320</td>
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</table>

Since hydrogen can be electrochemically inserted into and extracted from Pd-based electrodes, such materials can be treated as phase change-discharging systems. To characterize the material in the aspect of energy storage, one can consider in hydrogen absorption/extraction reactions pseudocapacitance. The values of specific pseudocapacitance (C°) were calculated for the process of electroreduction of hydrogen absorbed as the φ-phase (absorption potential in the range -0.1 to 0 V) according to the equation:

\[ C° = \frac{Q°_{pH2}}{C_{pH2}} \]

where Q°pH2 is the charge of hydrogen oxidation, C° is the potential range in which all absorbed hydrogen is electrochemically removed, and m is the mass of the material. The calculations were made for the mass of the electroactive material (i.e., Pd or Pd-Rh layer) as well as for the total mass (i.e., the sum of deposit and RVC substrate mass). These values are listed in Table 2.

Table 2. Pseudocapacitance Characteristics of Pd and Pd-Rh Hydrogen Absorbing Deposits on Various Substrates

<table>
<thead>
<tr>
<th>Electrode Material</th>
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As expected, the pseudocapacitance per total mass is lower than per electroactive mass. However, the former value of specific pseudocapacitance for Pd and Pd-Rh deposits on RVC is still comparable with the data reported for supercapacitors based on reasonable insertion of atomic species into the crystal structure of bulk solid electrolytes, e.g. polymers or BO₃ units and higher than values typical of double layer electrochemical capacitors. Although in this case of deposits on RVC electroplated with Au specific pseudocapacitance related to total mass in lower than the deposits on bare RVC, Au/RVC matrix seems to be more appropriate for real applications due to better deposit adherence to the substrate.

SUMMARY

Pd and Pd-Rh alloys can be potentiostatically deposited on RVC matrix. RVC substrate does not affect hydrogen absorption behavior of the deposits. The maximum values of hydrogen-to-metal ratio, HP/H₂+Pd+Rh, in the φ-phase are between 0.66-0.76. Pd-based layers deposited on RVC can be treated as phase change-discharging systems. The values of specific pseudocapacitance are in the range 130-540 F/g, i.e. comparable with those for supercapacitors utilizing various insertion reactions.

\[ \text{Potential vs. SHE (V)} \]

\[ \text{Deposit Bath composition} \]

RVC Au wire
or Au/RVC
Pd 0.11 M PdCl₂
1 M HCl 0.36 0.36
Pd-Rh (92-97 % Pd in the bulk) 0.09 M PdCl₂
0.08 M RhCl₃ 0.36 0.36
Au 0.07 M HAuCl₄ 0.36

Figs. 3 and 4 present the dependence of the electrochemically measured hydrogen absorption capacities, expressed as the hydrogen-to-metal ratio, on the absorption potential, for Pd and Pd-Rh alloys deposited on various substrates. This relationship has a characteristic shape, determined by the forms of hydrogen present in the system. At relatively high potentials (region 1), only absorbed hydrogen is hydrogen adsorbed as the φ-phase exist. Then a sharp increase in the amount of sorbed hydrogen is observed (region 2), which corresponds to the φ- phase transition. In lower potentials absorbed hydrogen stays as the φ-phase and its amount reaches a steady value (region 3). For Pd-Rh alloys the φ-phase transition is shifted slightly into a negative direction with respect to the case of pure Pd, which is a result of a smaller lattice parameter in the Pd-Rh system in comparison with Pd. Figs. 3 and 4 demonstrate that there is no qualitative influence of RVC substrate on the absorption behavior of Pd and Pd-Rh deposits. The amount of absorbed hydrogen was in a good agreement with the literature data.