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ARTICLE

Hydrogen Bubble Templated Co-deposition of Dendritic Porous PdAg Films and Electrocatalytic Activity

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Abstract: PdAg films with self-supported porous dendritic walls were fabricated by a hydrogen dynamic template method, in which transport channels could be provided by the micron-sized pores and the interstices between the dendrites. Different composition PdAg catalysts were obtained by adjusting the proportion of $Pd(NO_3)_2$ to $AgNO_3$ and the effect of the addition of Ag on the catalytic performance for ethanol was also studied. The cyclic voltammetry (CV) curves show that PdAg films possess high catalytic activity for ethanol and the addition of Ag significantly increases the mass-normalized catalytic activity of Pd. The mass-normalized catalytic current density of porous $Pd_{51}Ag_{49}$ is 0.49 A/mg, and it is estimated as 1.47 times as that of porous Pd. X-ray photoelectron spectroscopy (XPS) study indicates that the enhancement of the catalytic activity of PdAg films could be ascribed to the change of the Pd electronic structure when Ag atoms are embedded into the Pd lattice to form PdAg alloy as shown in X-ray diffraction (XRD) and element analysis mapping (EM) results.

Key words: hydrogen bubble template; porous dendrite; catalytic activity; PdAg films

As an important energy conversion device, direct ethanol fuel cell (DEFC) has attracted great interest due to the high energy conversion efficiency and environmental friendly property. Catalyst is the vital part in the direct fuel cell technology for its significant effects on the comprehensive catalytic performance. At present, Pt and Pt-based catalysts are still the mainstream electrocatalysts to facilitate the oxidation of fuel molecules (methanol, ethanol, etc.) for fuel cells. However, the Pt-based catalysts have many problems including high cost, self-poisoning by intermediates and so on, which would limit the catalytic performance and their application in direct fuel cell. Therefore, it is imperative to develop an effective and relatively low-priced substitute for Pt.

Compared with other metals, Pd has several advantages such as similar catalytic activity with Pt, relatively low price and well anti-CO poisoning ability, and therefore Pd is deemed as a suitable substitute for Pt catalyst^[1,2]. Besides, the catalytic activity of Pd-based catalysts could be further improved by alloying with another metal, for instance, Pd-Ni,

Pd-Au, and Pd-Fe^[3-5]. Due to the great energy difference between Ag and Pd in d-band center (Ag: -4.30 eV vs. Pd: -1.83 eV), Ag would be one of the most suitable elements to change the electronic structure of Pd based on d-band theory^[6]. Thus, the catalytic performance might be modified by the alloying Ag with Pd. Several researches have indicated that PdAg alloy nanowires^[7] and dendrities^[8] have better catalytic performance than pure Pd. However, the methods they used were quite complex, usually comprising a time-consuming process of the template removal. Therefore, some facile routes should be developed to prepare PdAg catalyst.

Hydrogen bubble templated electrodeposition (HBTE) is a facile approach to obtain 3D porous structure, which could greatly enhance the catalytic performance of the material. During the process, the reduced H_2 worked as dynamic template and simultaneously electrodeposited the metal ion to form the 3D porous material^[9]. Compared with other synthetic methods, HBTE technique possesses several advantages: low cost, high efficiency, free pollution, and facile handling. So far

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the HBTE technique has been successfully employed to fabricate different porous catalysts such as Cu, Ag, Pt, Pd, PtPd, and Ni/MnO_x^[10-15].

Thus, HBTE method was used in the present work to prepare dendritic porous PdAg films. The PdAg films with different compositions have been deposited on glass carbon electrodes (GCEs) by changing the molar ratio of two metal precursors in feeding solution. As a result, the Pd₅₁Ag₄₉ film exhibited the optimal catalytic activity for ethanol oxidation among all the prepared samples.

1 Experiment

Deposition baths and stock solutions for electroanalysis were prepared from deionized water. $Pd(NO_3)_2$, AgNO₃ and NH₄NO₃ (purchased in Shenyang Nonferrous Metal Research Institute) were high purity chemicals, used without further purification.

The porous Pd and PdAg films were synthesized on a CHI660E workstation (Chenhua Instruments, Shanghai, China) with three-electrode system. The glassy carbon electrode (d=4mm) served as the working electrode, the platinum foil as the counter electrode and saturated mercurous sulfate electrode (MSE) as the reference electrode. The GCE was polished with 0.05 µm alumina powder until a mirror-like surface was obtained. Oxygen in all solutions was removed by purging with N_2 for 20 min. The Pd and PdAg films were potentiostatically deposited on the pretreated GCE by applying a high cathodic overpotential of -4 V for 200 s. The electrolytes contained x mmol/L Pd(NO₃)₂, (4-x) mmol/L AgNO₃ (x=4, 3.6, 3.2, 2.8, 2.4), 1 mol/L NH₄NO₃ in 1 mol/L H_2SO_4 and the deposited porous films were denoted as a, b, c, d, and e, respectively. The actual atomic ratios determined by inductively coupled plasma (ICP, Optima 8500) of the obtained PdAg catalysts were shown in Table 1.

The microstructure of prepared films was observed by a scanning electron microscope (SEM, FEI inspect F50). Transmission electron microscopy, high angle angular dark field (HAADF) and element analysis mapping (EM) were carried out on a TEM, FEI Titan G2 60-300 (AC-TEM). The crystalline information of PdAg films was collected via an X-ray diffractometer (XRD, DX-2700) using Cu K α radiation (λ =0.154 06 nm). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific EscaLab 250Xi with Al K α radiation and the binding energies were calibrated by the containment carbon (C 1s=284.6 eV).

Table 1	Composition	of different l	PdAg porous	films
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Sample	Amount of $Pd/\mu g$	Amount of Ag/ μ g	Real composition
а	119.09	0	Pd
b	111.74	19.45	Pd ₈₅ Ag ₁₅
c	94.91	29.47	Pd ₇₆ Ag ₂₄
d	72.12	48.61	$Pd_{60}Ag_{40}$
e	62.02	60.05	$Pd_{51}Ag_{49}$

Electrochemical measurements including cyclic voltammetry (CV) and chronoamperometry (CA) were performed on a CHI660E workstation at room temperature. The platinum foil electrode was used as the counter electrode, a mercuric oxide electrode (Hg/HgO) as the reference electrode, and the as-prepared GCE as the working electrode. The prepared catalysts were characterized successively in 1 mol/L KOH and 1 mol/L KOH+1 mol/L C_2H_5OH at a scan rate of 50 mV·s⁻¹. The CA curves were recorded under a constant potential of -0.1 V vs. Hg/HgO.

2 Results and Discussion

2.1 Morphology of the porous Pd and PdAg films

Firstly, the porous Pd films were deposited from the electrolyte containing 4 mmol/L Pd^{2+} and 1 mol/L H_2SO_4 at -4 V for 200 s, and their typical SEM images are shown in Fig.1a, 1e. From Fig.1a it could be seen that the film has an average pore size of 20 μ m as shown in Table 2. Fig.1e shows the porous wall consisted of dendrites with nanoparticles in all directions.

However, severe cracks will form due to bubble coalescence and anomalous co-deposition when AgNO3 was added into the aforementioned electrolyte to prepare PdAg alloy films. According to a previous study^[16], the addition of inorganic salt could change the surface tension of the gas-liquid interface. Suitable additive will affect bubble behavior by impeding the coalescence of the bubbles and thus reduce the cracks. NH₄NO₃ was chosen based on the aforementioned electrolyte. Fig.1b, 1f, 1c, 1g and 1d, 1h shows the SEM images of Pd₇₆Ag₂₄ film with 0.25, 0.5 and 1.0 mol/L NH₄NO₃, respectively. In Fig.1b, severe cracks divide the sample into pieces. In Fig.1c, although there are still some cracks, the whole sample exhibits better integrated morphology. When NH₄NO₃ concentration rised to 1.0 mol/L, the cracks could hardly be noticed. Besides, the addition of NH₄NO₃ will not affect the micro- scaled structure of the PdAg films and the size of the nanoparticles merely change with the increase of NH₄NO₃ concentration, as shown in Fig.1f, 1g, and 1 h.

PdAg films with different composition were prepared via co-deposition with 1 mol/L NH₄NO₃ in the aforementioned electrolytes and their morphology are shown in Fig.2. It could be seen that the PdAg films consist of macro-sized pores and self-supported porous walls. The corresponding magnified SEM images show that the porous structures comprise numerous dendrites in all directions, which construct the self-supported film. The top pore-size ranges are shown in Table 2 and there exist 200~300 nm interstices between different dendrites which may serve as the transport channel of electroactive species, leading to better utilization of the activated surface^[17]. The microsized pore and interstices between dendrites could indicate that the films are 3D connected. Detailed information about the morphology and grain size are shown in Fig.3. Fig.3a and Fig.3b are the



Fig.1 SEM images of porous Pd (a, e) and Pd₇₆Ag₂₄ films with different concentrations of NH₄NO₃: (b, f) 0.25 mol/L, (c, g) 0.5 mol/L, and (d, h) 1.0 mol/L



Fig.2 SEM images of porous PdAg alloy films with different composition co-deposited with 1 mol/L NH₄NO₃: (a) Pd₈₅Ag₁₅,
 (b) Pd₇₆Ag₂₄, (c) Pd₆₀Ag₄₀, and (d) Pd₅₁Ag₄₉

Table 2	Pore size of porous	s films with	different composition
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Composition	Pore-size range/µm	Average pore size/µm
Pd	13~30	20
Pd ₈₅ Ag ₁₅	6~13	11
$Pd_{76}Ag_{24}$	6~14	11
$Pd_{60}Ag_{40}$	6~15	11
$Pd_{51}Ag_{49}$	6~18	12

dendritic feature of Pd and $Pd_{76}Ag_{24}$ catalyst, respectively, and their dendritic feature is similar to each other. The average

grain size of Pd and PdAg are 20 and 15 nm, respectively, which indicates that the addition of Ag element could decrease the catalyst particle size slightly. The dendritic structure as shown in TEM could promote the mass transport rate, thus leading to better catalytic performance.

2.2 Composition of porous Pd and PdAg films

Fig.4 shows the XRD patterns and the enlarged peaks for the (111) plane of Pd and PdAg films. The diffraction peaks of pure Pd shows a typical face centered cubic (fcc) structure



Fig.3 TEM images of the as-prepared catalysts: (a) Pd, (b) Pd₇₆Ag₂₄; (c~f) HAADF images and the corresponding element analysis mapping of Pd₇₆Ag₂₄



Fig.4 XRD patterns of the as-prepared Pd and PdAg porous films and enlarged XRD patterns in the range of $38^{\circ} < 2\theta < 42^{\circ}$

with five diffraction peaks at 40.03°, 46.83°, 67.88°, 82.31° and 87.01°, which are corresponding to the (111), (200), (220), (311) and (222) planes, respectively. The diffraction peaks of PdAg also have an fcc structure, in which the peaks are located between the corresponding peaks of pure Pd and Ag (JCPDS #04-0783), suggesting the formation of PdAg alloys. From the magnified pictures, it can be clearly seen that the peaks shift to pure Ag gradually with the increasing of Ag content. It indicates that more and more Ag atoms are embedded into the Pd lattice to form PdAg alloy with the increased Ag⁺. Fig.3c~3f are high-angle annular dark field (HAADF) image and the corresponding EM of Pd₇₆Ag₂₄ catalyst. The EM results manifest the uniform distribution of Pd and Ag in the prepared $Pd_{76}Ag_{24}$, corroborating the formation of PdAg alloys.

To investigate the possible electronic effects on prepared PdAg films, the XPS valence band spectra of Pd and PdAg were collected and are shown in Fig.5. Both Pd 3d spectrum and Ag 3d spectrum comprise a low energy band (Pd 3d_{5/2}, Ag 3d_{5/2}) and a high energy band (Pd 3d_{3/2}, Ag 3d_{3/2}). The binding energies (BEs) of Ag increase gradually with the increase of Ag content. On the contrary, the BEs of Pd decrease with the increase of Ag content, which is consistent with the earlier research^[18]. As is well known, Pd has a full-filled 4d band and Ag has a half-filled 4s band which can either provide or accept an electron depending on the coordinate metal. Therefore, electrons will tend to flow from Pd 4d band to Ag 4s band in the interface, which would result in the electronic disturbance of Pd surface^[19], and further induce the d-band center shift from Fermi level when PdAg alloy is formed. As a result, the chemisorptions between adsorbate (CH₃CO_{ads}) and Pd surface will be weakened, which may benefit the electrooxidation of ethanol^[20].

2.3 Electrocatalytic activity of the porous Pd and PdAg films for the oxidation of ethanol

Fig.6a shows the CVs of the Pd and PdAg films in 1.0 mol/L KOH at a scan rate of 50 mV·s⁻¹. The peaks appearing at about -0.8 V are due to H adsorption and absorption onto and into Pd. The peaks emerge at -0.35 V in reverse scan are the reduction peak of palladium oxides which can be adopted to evaluate the actual electrochemical active surface areas (ECSAs) of Pd through Eqs. (1) and (2)^[3,21]. *Q* is the total charge during the reduction of PdO, which can be figured out



Fig.5 XPS spectra of prepared Pd and PdAg films for Pd 3d peaks (a) and Ag 3d peaks (b)

using integral area of PdO (*S*) and the scanning speed (*V*) by Eq. (1). The constant *C* is usually considered to be 4.24 $C/m^{[2,22]}$, which means the total amount of charge required to reduce PdO per square meter. And the electrochemically active surface area (ECSA) of unit mass can be calculated by Eq. (2). In the present study, the ECSA is 47.9, 42.5, 53.3, 63.0 and 64.1 m² (corresponding to Pd, Pd₈₅Ag₁₅, Pd₇₆Ag₂₄, Pd₆₀Ag₄₀, and Pd₅₁Ag₄₉, respectively) which rises as the increasing of Ag content except Pd₈₅Ag₁₅.

The CV curves of ethanol oxidation on different PdAg porous catalysts in 1.0 mol/L KOH+1.0 mol/L C2H5OH solution at a scan rate of 50 mV·s⁻¹ are shown in Fig.6b. The peaks located at -0.1 V in forward scan is the oxidation of palladium and the peaks appearing at -0.3 V in reverse scan is considered as the removal of intermediate species^[23]. The oxidation peak in the forward scan is usually used to evaluate the electrocatalytic activity of catalysts because pure Ag is not active for electrocatalytic reaction in alkaline media^[5]. In our study, the mass-normalized current density of porous Pd is 0.32 A/mg in the forward scan and the peak current density increases with the increasing of Ag content except Pd₈₅Ag₁₅. Because the catalytic activity increased by alloving cannot offset the decreasing ECSA as the specific value mentioned above. The mass-normalized current density of Pd₅₁Ag₄₉ catalyst is the highest, 0.49 A/mg, almost 1.47 times of that of



Fig.6 CV curves for the Pd and PdAg in 1.0 mol/L KOH (a) and in 1.0 mol/L KOH containing 1.0 mol/L C₂H₃OH (b)

porous Pd. It possesses higher current density than porous PdNi catalyst whose mass-normalized catalytic activity is 0.238 A/mg (0.5 mol/L KOH+0.5 mol/L CH₃OH)^[3]. The result indicates the incorporation of Ag into Pd can improve the mass-normalized catalytic activity for ethanol oxidation and the enhanced activity could mainly be attributed to the geometric and electronic effect. On the one hand, porous structure could act as the channel of mass transfer and the larger ECSA of PdAg catalysts than that of Pd could provide more active sites for ethanol due to the addition of Ag. On the other hand, the shift of d-band center, which results from the structure changing by addition of Ag, could reduce the reaction energy of ethanol oxidation.

2.4 Electrochemical stabilities of the Pd and PdAg films for ethanol oxidation

The catalytic stabilities for ethanol electro-oxidation of Pd and PdAg films were studied by processing CA tests at -0.1 V in 1.0 mol/L KOH+1.0 mol/L C₂H₅OH. Fig.7 shows that all samples have the similar curves and Pd₆₀Ag₄₀ has the highest current stabilities for ethanol oxidation. At the beginning, the curves of all catalysts plummet and then decline gradually with prolonged time. This catalystic stability of Pd-based catalysts may result from the strong tolerance against intermediate species such as CH₃CO_{ads} and CO^[24]. Seen from Fig.7, the current density of Pd₅₁Ag₄₉ decreases more rapidly than those of any other samples. This might be ascribed to the relatively dense 3D porous structure of the Pd₅₁Ag₄₉ sample (see Fig.2d) and restricts its long-term stability.



Fig.7 Chronoamperograms of Pd and PdAg catalysts (1.0 mol/L KOH+1.0 mol/L C₂H₅OH, -0.1 V vs. Hg/HgO)

3 Conclusions

1) Dendritic porous Pd and PdAg catalysts were synthesized via a hydrogen dynamic bubble template method. The cracks could be efficiently mitigated due to the addition of NH_4NO_3 .

2) The PdAg films show enhanced catalytic activity for ethanol electrooxidation in alkaline medium and mass-normalized catalytic activity of $Pd_{51}Ag_{49}$ (0.49 A/mg) is 1.47 times of that of porous Pd.

3) The enhanced activity can be ascribed to the special structure and the change of electronic structure via alloying Ag into Pd lattice.

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氢气泡制备枝晶状多孔钯银薄膜及其催化性能

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摘要:通过氢气泡动态模板法制备了具有多孔枝晶壁的钯银合金薄膜,微米级的大孔和枝晶间的间隙提供了反应过程中的介质传输通道。调节硝酸钯和硝酸银的配比制备了不同成分的钯银合金薄膜且研究了银的添加对催化性能的影响。循环伏安(CV)曲线表明钯银合金具有高的催化活性且银的添加可提高单位质量钯的催化活性,其中多孔 Pd₅₁Ag₄₉的催化电流密度为 0.49 A/mg,是多孔钯的 1.47 倍。X 射线光电子能谱(XPS)结果说明钯银薄膜催化活性的提高可归因于钯银合金形成时银原子进入钯晶格间隙引起的钯电子结构的改变,X 射线衍射(XRD)谱图和元素面扫(EM)结果也说明了合金的形成。
 关键词:氢气泡模板;多孔枝晶;催化性能;钯银薄膜

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