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Binary platinum alloy electrodes for hydrogen and oxygen evolutions by seawater splitting

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ABSTRACT

Hydrogen and oxygen evolutions by seawater splitting are persistent objectives for green energy production. We present here the experimental realization of Ti foil supported PtM (M = Fe, Co, Ni, Pd) alloy electrodes by a cycle voltammetry method for seawater splitting. The preliminary results demonstrate that the resultant Ti supported PtM alloy electrodes are robust in realizing high-efficiency hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), arising from enhanced current density, reduced potential, and good durability. By tuning M species, the Ti supported PtPd alloy electrode displays a maximal efficiency, yielding an onset potential of −52 mV and 690 mV (*vs* RHE) in HER and OER, respectively. The current densities of Ti supported PtPd electrode are as high as 270 mA cm^{-2} at 1.32 V (*vs* RHE) and 590 mA cm^{-2} at 3.99 V (*vs* RHE). Moreover, the long-term stability has also been increased by alloying Pt with M. Although the work presented here is far from optimized, the concept of alloying transition metals with Pt can guide us to design highly efficient alloy electrodes for hydrogen and oxygen evolutions from seawater splitting.

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1. Introduction

Hydrogen energy has attracted growing attention as a renewable energy resource owing to its merits on environmental friendliness, high-efficiency, and gigantic storage in ocean [1,2]. Electrochemical water splitting is considered as one of the most promising strategies for hydrogen evolution [3–6]. During the water splitting for hydrogen evolution, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are two crucial electrochemical processes, and precious platinum (Pt) species are always preferred electrocatalysts. Although Pt electrode is honored with high-efficiency and long-term stability, the high cost has been an economic burden for their commercial applications. For the sake of cost-effective electrocatalysts without sacrificing electrochemical performances, many alternatives such as oxides [7,8], sulfides [9,10], nitrides [11–13], carbides [14], phosphides [15–17], selenides [18,19], alloys [20,21], carbonaceous materials [22], conducting polymers [23] and composite materials [24–27] have been successfully developed in the past decades. Despite great efforts are made in creating cost-effective and high-efficiency electrocatalysts for water splitting, the HER has not yet accelerated in comparison with preferred Pt species. The reasonable electrocatalytic activity of Pt mainly arises from its *d*-band electronic density [28], nearly zero for ΔG-H_{ads} [29], and 1.57 eV for ΔE_o [30]. Therefore, the alloying of Pt with cost-effective transition metals to form low-Pt alloy catalysts is considered as one of the promising methods for advanced electrocatalysts, arising from alloy effect between Pt and transition metals.

The transition metals exhibit a Sabatier trend in HER electrocatalytic activity (yielding a so-called "volcano" plot) and good behaviors in ORR electrocatalytic properties, which are shown in Fig. 1. In accordance with the theoretical predictions [31], Pt and its group metals have the highest activity in HER (in Fig. 1a) [32] and ORR (in Fig. 1b) [33]. Notably, transition metal such as Ni, Co, or Fe is also available for water splitting. For example, Ni and Co have the same ΔE_H (−0.51 eV), which is approaching to that of Pt (−0.33 eV). In addition, the ΔE_o values of Ni and Co are 0.34 and −0.22 eV, respectively, which are much lower than 1.57 eV for Pt. Therefore, the alloying of Pt with transition metal such as Ni, Co, or Fe may create cost-effective but robust electrocatalysts for water splitting.

To realize efficient hydrogen evolution, acids or alkalis are always added into pure water to increase ionic conductivity, raising specific requirements for electrocatalysts such as good resistance to corrosion and oxidation. This increases the complexity of techniques and demands for selecting electrode species. One of the

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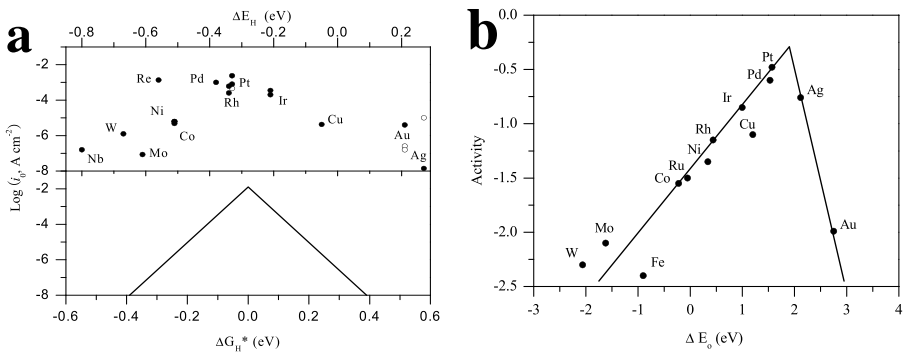

Fig. 1. (a) Experimental exchange current and log (i_0) for hydrogen evolution at different transition metals plotted as a function of the calculated hydrogen chemisorption energy per atom (ΔE_H) and the free energy for hydrogen adsorption ($\Delta G_{H^*} = \Delta E_H + 0.24$ eV), reproduced from Ref. [21]; (b) Theoretical activity toward ORR plotted as a function of the oxygen binding energy (ΔE_O).

solutions to this impasse is to replace acidic or basic solutions with neutral seawater because of the following three advantages: (i) ~70% surface of the earth is covered by ocean, therefore the seawater splitting is promising for sustainably creating hydrogen energy; (ii) Seawater is similar to 0.6 M sodium choloride aqueous solution, providing high ionic conductivity for realizing loop during electrolysis process; (iii) Seawater is neutral, it has low corrosion to catalytic electrodes.

For the sake of searching cheaper electrodes without sacrificing electrocatalytic performances, we present here an experimental realization of titanium (Ti) foil supported PtM (M = Fe, Co, Ni, Pd) alloy electrodes by a simple cyclic voltammetry deposition strategy. The corresponding measurements are performed in a real seawater (pH = 6.64, ionic conductivity = 33.9 mS cm^{-1}, T = 25 °C). The preliminary results demonstrate that the resultant Ti supported PtM alloy electrodes have high electrocatalytic activity and excellent corrosion resistance.

2. Experimental

2.1. Preparation of PtM alloy electrodes

Prior to deposition, the Ti substrate with a thickness of 1 mm was pretreated. In details, Ti foil was cut into 5 cm × 5 cm, and immersed in acetone solution with ultrasound for 15 min. After being thoroughly rinsed with deionized water, the Ti substrate was soaked into 1 M of oxalic acid aqueous solution at 95 °C for 2 h and finally rinsed with deionized water.

Ti supported PtM (M = Fe, Co, Ni, Pd) alloy electrodes were realized by a cycle voltammetry (CV) strategy on a traditional three-electrode electrochemical workstation (CHI660E). The pretreated Ti foil was used as a working electrode, a Pt plate was a counter electrode, and an Ag/AgCl was a reference electrode. The supporting electrolyte was composed of 10 mL of 0.2 mM chloroplatinic acid (H_2PtCl_6) and 10 mL of 0.6 mM metal salt aqueous solution ($CoCl_2$, $NiCl_2$, $FeCl_3$, $PdCl_2$) with a molar ratio of 1:3 for Pt/M. The CV curves were recorded from −0.6 to 1.4 V and then back to −0.6 V for ten cycles. Finally, the PtM alloy electrodes were rinsed with deionized water and dried by nitrogen gas.

2.2. Electrochemical characterizations

All the electrochemical measurements were recorded on an electrochemical workstation (CHI660E) with a three-electrode mode in seawater: a Pt plate as a counter electrode, an Ag/AgCl electrode as reference electrode and fabricated electrode as working electrode. The potential measurements were converted to the reversible hydrogen electrode (RHE) based on the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197$. The CV curves were recorded from −0.25 to 1.9 V (*versus* the RHE) and then back to −0.25 V. The linear sweep voltammetry curves were scanned from −1.2 to 0.6 V (*vs* the RHE) for HER and from 0.5 to 4.5 V (*vs* the RHE) for ORR in a supporting electrolyte of seawater at a scan rate of 1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was also measured in a frequency ranging from 0.1 to 10^6 Hz with an ac-amplitude of 5 mV. Tafel polarization curve was recorded from −0.6 to 2.5 V (*vs* the RHE) at a scan rate of 10 mV s^{-1}.

2.3. Other characterizations

The surface morphologies of alloy electrodes were determined on a scanning electron microscope (SEM, S4800). X-ray photoelectron spectroscopy (XPS) experiment was carried out on a thermo ESCALAB 250Xi (form America) with Al Ka (hv = 1486.6 eV). The X-ray diffraction (XRD) analysis of the samples was performed with a Bruker D8 Advance powder diffractometer with CuKa radiation (λ = 1.54056 Å). The PtPd catalyst was characterized by a transmission electron microscopy (TEM, JEM2010, JEOL).

3. Results and discussion

The composites of final PtM catalysts were confirmed by ICP-AES measurement, yielding atomic ratios of 2.791: 1.000, 3.105: 1.000, 3.185: 1.000 and 3.402: 1.000 for PtFe, PtCo, PtNi and PtPd, respectively. Fig. 2 shows the XRD patterns of Ti supported Pt and PtM (M = Fe, Co, Ni, Pd) alloy electrodes, yielding (101), (102), and

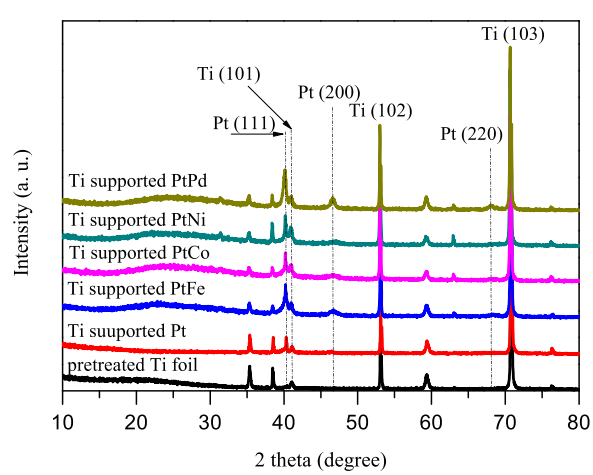

Fig. 2. The XRD profiles of Ti supported Pt and PtM (M = Fe, Co, Ni, Pd) alloy electrodes.

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