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AgSn intermetallics as highly selective and active oxygen reduction electrocatalysts in membraneless alkaline fuel cells

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HIGHLIGHTS

- AgSn intermetallics were successfully synthesized by an electrochemical method.
- AgSn intermetallics exhibited excellent ORR activity and stability.
- AgSn intermetallics showed superior tolerance to alcohol than commercial Pt/C.
- High catalytic properties are attributed to ensemble effect and ordered structure.
- Membraneless alkaline fuel cells based on selective catalysts were designed.

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ABSTRACT

The Ag_4Sn and Ag_3Sn intermetallics are successfully synthesized by combining electrochemical deposition and dealloying methods. The Ag_4Sn and Ag_3Sn possess a half-wave potential of 0.810 mV and 0.790 mV respectively for the oxygen reduction reaction in alkaline media, which are comparable to the commercial Pt/C (0.837 mV). In term of the durability, the Ag_4Sn retains a half-wave potential of 0.775 mV after 5000 potential cycles, which is superior to Pt/C of 0.784 mV. The better catalytic activity and durability are mainly attributed to the ensemble effect and strong chemical bond in the AgSn ordered intermetallic structure. The catalytic activity is hardly influenced by methanol or ethanol in alkaline media with alcohol concentrations up to 1.0 M. Therefore, a membraneless alkaline zinc-air battery and direct alcohol fuel cell can operate with Ag_4Sn and Ag_3Sn intermetallics as the cathode catalysts, which allow the anode fuel to freely enter the cathode. A high power density is delivered by the membraneless alkaline fuel cells with zinc, methanol or ethanol as anode fuels. The excellent alcohol-tolerance is beneficial to the oxygen reduction reaction of alkaline fuel cells and makes the AgSn intermetallics a promising candidate to replace Pt-based electrocatalysts for oxygen reduction reaction.

1. Introduction

The alkaline fuel cells have been developed to meet rapidly rising energy demand and to resolve environmental issues owing to their fascinating features, including large energy density, high energy efficiency, easy storage/transportation, and low/zero emission [1–5]. In comparison to the acid fuel cells, they also offer the facile kinetics of electrode reaction and avoid the corrosive problems of catalysts, especially using the transition metals (e.g. Fe, Co, Ni, Cu) [6]. For the alkaline fuel cells, an anion-exchange membrane is necessary to separate the anode and the cathode while providing OH^- migration [7]. More importantly, this membrane can prevent the crossover of fuel and oxidant between the anode and cathode to maximize the power output of the fuel cell [8]. However, the state-of-the-art anion-exchange membranes still suffer from the poor ionic conductivity, the limited stability, the high rate of alcohol crossover and the lack of industrial production [9,10]. On the other hand, the use of the membrane severely restricts the device design, limits the electrolyte choice and increases the cell cost. Therefore, a membraneless alkaline fuel cell that avoids the above obstacles has recently attracted much attention.

As far as we are aware, the membraneless alkaline fuel cells can be divided into two types: laminar flow-based fuel cells and fuel cells with

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alcohol-tolerant cathode catalysts. Laminar flow-based fuel cells are difficult to be scaled up for a single cell due to the millimeter-scale size [11]. Even through improving cell designs, stacking or multiplexing technology, this type of membraneless fuel cells are not yet satisfactory for the practical applications in terms of power and cost [12–14]. Hence, the membraneless alkaline fuel cells mainly based on alcohol-tolerant cathode catalysts are of particularly interest, which achieve more flexibility and miniaturizability in cell design, simpler implementation, and low cost. Central to the operation of all the membraneless alkaline fuel cells is the efficient, alcohol-tolerant oxygen reduction reaction (ORR) catalyst. In spite of the prohibitive cost and low reserves [15], in addition to the sluggish kinetics and poor durability [16,17], platinum (Pt) is the most popular electrocatalyst for the ORR in alkaline fuel cells, but their ORR performances are easily degraded due to the mixed-potential and catalyst poisoning forming at the cathode. This is because Pt catalyst is also catalytically active toward alcohols so that the serious alcohol crossover through the membrane leads to the significant decay of the cell performance [18–20].

Considerable efforts and progresses have been made to develop the alcohol-tolerant Pt-based ORR catalysts [21–28]. For instance, Guo and co-workers [22] reported a PtBi intermetallic nanocatalyst, which offers an excellent methanol tolerance but a lower ORR activity than that of the commercial Pt/C catalyst. Jeyakumar group [23] developed the $Au_{85}Pt_{15}/C$ catalyst, which showed both excellent methanol tolerance behavior and better ORR performance in terms of the mass activity and power density in a single fuel cell as compared to that using the commercial Pt/C catalyst. Cho et al. [24] prepared the PtPdCo/C ternary electrocatalysts, which exhibited a similar ORR activity and superior methanol tolerance as compared to Pt/C. The PtPd nanoflowers [25], PtNi intermetallics [26], Pt nanoparticles on $CoSe_2$ nanobelts [27], and Pt nanoparticles encapsulated in nitrogen-doped carbon nanocages [28] were found to be insensitive to methanol so that they display an improved methanol tolerance performance and can be used for alcohol-tolerant ORR catalysts.

However, such Pt-based ORR electrocatalysts still show relatively low methanol tolerance due to the limited suppression of alcohol oxidation reaction (AOR). To address this issue, recent research has been focused on Ag-based alcohol-tolerant catalysts, which have a much lower cost than Pt-based catalysts. As compared with Pt-based catalysts, the Ag-based catalysts possess a similar ORR mechanism and kinetics but a higher tolerance to alcohol [29–31]. Currently, Ag and Ag-based alloys exhibit good alcohol-tolerant capability while maintain high ORR activity. For instance, Zeng and Ni et al. [32,33] reported the Ag nanowires exhibited a good activity and alcohol-tolerant stability for the ORR in alkaline media. Lu et al. [34] reported that Ag_4Sn intermetallic nanoparticles displayed better ORR performance and excellent tolerance to methanol, but no durability test was investigated. In our previous work, we have found that the Ag_3Sn nano-intermetallic can be used as a good bifunctional electrocatalyst for ORR and borohydride oxidation reaction (BOR) [35]. Taylor et al. [31] synthesized a silver palladium core-shell catalyst on multiwall carbon nanotubes by galvanic displacement of Pd on Ag nanoparticles, the Ag@Pd catalysts showed a high ORR activity and alcohol-tolerant capability in the presence of methanol and ethanol. In the presence of methanol, the current density on Ag@Pd decreased by $0.18\ mA/cm^2$, compared to Pt/C ($0.97\ mA/cm^2$) and Pd/C ($1.09\ mA/cm^2$). Unfortunately, the state-of-the-art Ag-based alcohol-tolerant catalysts demonstrate a lower ORR activity and inferior long-term stability in comparison to Pt-based catalysts.

In this work, we develop the novel AgSn intermetallic catalysts with different compositions and morphologies, synthesized via combining electrochemical deposition and dealloying methods. The precursor alloys with various surface morphology and elemental compositions are prepared by tuning the deposition current, afterwards, the pure phase Ag_4Sn and Ag_3Sn intermetallic catalysts are obtained by dealloying in diluted $HClO_4$. The Ag_4Sn and Ag_3Sn catalysts possess a half-wave potential of 0.810 mV and 0.790 mV for the ORR activity, which is comparable to the commercial Pt/C catalyst. The Ag_4Sn exhibits superior stability with only 35 mV shift in $E_{1/2}$ after 5000 potential cycles. More importantly, this AgSn intermetallic with relatively high ORR activity is insensitive to alcohol crossover into the cathode and performs well at high alcohol concentration, which makes it promising to exclude the alkaline anion-exchange membrane from the cell. Building on the promising selective ORR activity in the presence of the alcohol, three membraneless alkaline fuel cells are demonstrated with zinc, methanol, and ethanol as anode fuels.

2. Experimental

2.1. Preparation of samples

2.1.1. Electrodeposition of precursor alloy

The Ag_xSn_{100-x} alloy was synthesized using a three-electrode system containing a glassy carbon working electrode, platinum sheet counter electrode and saturated calomel electrode (SCE) reference electrode. The electroplating solution was composed of 2.0 M H_2SO_4, 0.2 M $SC(NH_2)_2$, 0.025 M $SnSO_4$, and 0.01 M Ag_2SO_4. Electrodeposition was carried out galvanostatically with mild agitation until the quantity of electricity approached to $0.3\ mC\ cm^{-2}$. The $Ag_{75}Sn_{25}$ and $Ag_{50}Sn_{50}$ precursor alloys were deposited at a current density of 10.2 and $25.5\ mA\ cm^{-2}$, respectively, whose atomic ratios of Ag/Sn were measured by the energy-dispersive X-ray spectrometer of scanning electron microscopy. The as-synthesized alloys were washed with DI water, and then dried in nitrogen at room temperature.

2.1.2. Dealloying of precursor alloy

To remove Sn and adjust the Ag/Sn ratio, the electrochemical dealloying was conducted within a potential range of −0.45 V to 0 V in a N_2-purged 0.1 M $HClO_4$ solution at a scan rate of $50\ mV\ s^{-1}$ for several cycles.

2.2. Physical characterization

The morphology, structure, and composition of the samples were characterized by a field-emission scanning electron microscopy (FESEM, FEI NovaSEM 450) with an energy-dispersive X-ray spectrometer (EDX) detector, and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30), X-ray diffraction (XRD) (PANalytical X'Pert Pro MPD, Cu Kα radiation of 1.5406 Å), and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250).

2.3. Electrochemical characterization

Electrochemical investigations were carried out at room temperature using CHI 660C electrochemical workstation (Chenhua, China). The working electrode was prepared by electrodepositing the catalyst on the glassy carbon rotating disk electrode (GC-RDE, 5 mm in diameter). Pt wire and Hg/HgO electrode were used as the counter and reference electrodes, respectively. All potentials in this paper were reported relative to the reversible hydrogen electrode (RHE) unless indicated. The ORR activities of the catalysts were examined in 0.1 M KOH solution saturated with oxygen. Linear scanning voltammetry (LSV) curves at different rotation rates were performed with a scan rate of $10\ mV\ s^{-1}$. The alcohol tolerances (methanol and ethanol) were examined by adding alcohols at different concentrations (ranging from 1 mM to 1 M) to the alkaline electrolyte saturated with oxygen. The ORR response in the presence of alcohols was obtained at a scan rate of $10\ mV\ s^{-1}$ and at a rotation speed of 1600 rpm. For comparison, the commercial Pt/C (Johnson Matthey, 20 wt. %) was also tested. The electrochemical surface area (ECSA) of Ag-based materials was measured using Pb-stripping voltammetry. Pb-stripping voltammetry was conducted by holding the potential at 0.20 V and then sweeping to