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Comparison of electrocatalytic activity of carbon-supported Au–M (M = Fe, Co, Ni, Cu and Zn) bimetallic nanoparticles for direct borohydride fuel cells

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ARTICLE INFO

Article history:

Received 2 February 2012

Received in revised form

30 April 2012

Accepted 14 May 2012

Available online 9 June 2012

Keywords:

Direct borohydride fuel cell

Bimetallic nanoparticles

Electrocatalysis

Catalytic activity for borohydride oxidation

ABSTRACT

The Au–M (M = Fe, Co, Ni, Cu and Zn) bimetallic nanoparticles supported on the Vulcan XC-72R (Au–M/C) were synthesized by a reverse micelle method. The structures and compositions of the carbon supported Au–M catalysts were characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDS). The electrocatalytic activity of the Au–M bimetallic nanoparticles with respect to borohydride electro-oxidation for the application of fuel cell was investigated by voltammetry, chronoamperometry and chronopotentiometry. The results showed that alloying Au with 3d transition metals Fe, Co, Ni, Cu or Zn, a metal that leads to the maximum eight-electron oxidation of BH₄[−], not only improved the electrode kinetics of BH₄[−] oxidation but also reduced catalyst cost. Among the various investigated Au–M/C electrocatalysts, the Au–Zn, Au–Fe and Au–Cu catalysts showed no activity of NaBH₄ hydrolysis, and Au–Zn presented an attractive catalytic activity for borohydride oxidation.

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1. Introduction

Direct borohydride fuel cell (DBFC) has been hailed as an important power source for the future because of its high energy density with low pollution [1–8]. In the electrochemical oxidation of sodium borohydride, the electrode material is a key factor for a highly efficient electrocatalyst. Bimetallic nanoparticles are of wide interest since they lead to many interesting size-dependent electrical, chemical and optical properties. They are particularly important in the field of catalysis since they often exhibit better catalytic properties than their monometallic counterparts [9–15]. The bimetallic nanoparticle catalysts usually consist of a primary metal that has a high efficiency in electrocatalyst and a secondary metal

that can either enhance the catalytic activity of BH₄[−] oxidation or inhibit BH₄[−] hydrolysis. It was well reported that high coulombic numbers near 8e[−] were obtained by using Au anodes due to its inactivity towards the hydrolysis reaction [16,17,45,46]. It has been used in conjunction with metals such as palladium [12,13,18–29], osmium and platinum [15,21,26,30–34] for catalytic oxidation reactions of BH₄[−]. However, the 3d transition metals (Fe, Co, Ni, Cu, Zn), which are cheaper than palladium and platinum, haven't received extensive attention. Since the 3d transition metals with the unoccupied 3d orbital which might be propitious to enhance the electrochemical activity of bimetallic catalyst for BH₄[−] oxidation and cut down the price of electrocatalyst, it is worth to systematically discuss the effects and phenomena of the

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carbon-supported Au alloying 3d transition metals (Fe, Co, Ni, Cu, Zn) for electrochemical activity of BH_4^- oxidation. In our previous works, we have successfully prepared Au–Co, Au–Ni and Au–Zn bimetallic catalysts with different ratios, and found that the catalysts gave the excellent electrochemical performance for DBFC [9,35–37]. Based on our previous works [35,36], in this study we will prepare Au–M/C ($M = \text{Fe, Co, Ni, Cu}$ and Zn) electrocatalysts with the original input atomic ratio of 1:1, compare systemically their electrocatalytic activity and reactivity kinetics for BH_4^- oxidation.

2. Experimental

2.1. Preparation of carbon-supported Au–M (Fe, Co, Ni, Cu, Zn) nanoparticles

The Au–M/C ($M = \text{Fe, Co, Ni, Cu, Zn}$) electrocatalysts were synthesized by a reverse microemulsion method using sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as the surfactant and heptane as the oil phase. The detail procedures were reported in our previous work [36]. Briefly, appropriate amounts of HAuCl_4 and M_xCl_y (Au–M, 1:1 atomic ratio) were added into 0.1 M AOT/n-heptane solution. The sodium borohydride reverse microemulsion flowed into the metal salts reverse microemulsion. In the same time, high purity argon gas was bubbled through the reaction system to remove the dissolved oxygen. Subsequently, an appropriate amount of Vulcan XC-72R carbon was added and the Au–M/C powder was filtrated and dried. Finally, the powder was heated in an atmosphere of 10% H_2 -90% Ar for 2 h.

2.2. Characterization of Au–M/C electrocatalysts

The Au/M atomic ratios of Au–M/C electrocatalysts were determined by Powder energy dispersive spectra (EDS) analysis. X-ray diffractometer (D/MAX-3C) was employed with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator at 50 kV, 100 mA, to obtain X-ray diffraction (XRD) patterns of the samples. The 2θ angular regions between 10° and 120° were explored at a scan rate of 8° min^{-1} .

2.3. Electrochemical performance of anode catalysts

The Au–M/C working electrode was prepared as follows: 10 mg Au–M/C electrocatalyst was dispersed by ultrasonic for 2 h in 1 ml solution composed of 0.25 ml 5% Nafion solution and 0.75 ml distilled water. Then 5 μl of suspension was carefully applied on glassy carbon (GC) (3 mm in diameter) electrode surface. The dispersed Au–M/C electrocatalyst on the GC surface was dried at room temperature. The loading mass of Au/C or Au–M/C electrocatalyst was 0.7 mg cm^{-2} .

A conventional three-electrode system was used to perform the electrochemical tests. The system was composed of the Au–M/C working electrode, a Ni foam mesh with $3 \times 5 \text{ cm}^2$ surface area as the counter electrode and an Ag/AgCl, KCl_{std} as the reference electrode. Voltammetry, chronopotentiometry and chronoamperometry experiments were conducted with a CHI660A Electrochemistry Workstation.

3. Results and discussion

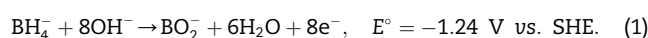
3.1. Characterizations of the structures for various Au–M ($M = \text{Fe, Co, Ni, Cu, Zn}$) electrocatalysts

In order to determine the chemical composition of the Au–M ($M = \text{Fe, Co, Ni, Cu, Zn}$) electrocatalysts the energy dispersive spectrometry (EDS) was used. Fig. 1 shows the powder energy dispersive spectra for Au–M electrocatalysts corresponding to a randomly selected zone in the powder sample indicated in the inset. All the EDS Spectra showed the characteristic peaks for Au, carbon and alloying elements. It can be found that the atomic ratios of Au and alloying elements are nearly 1:1, for example, 51:49, 45:55, 58:42, 50:50 and 50:50 for Au–Fe, Au–Co, Au–Ni, Au–Cu and Au–Zn, respectively. The element ratios of Au and M ($M = \text{Fe, Co, Ni, Cu, Zn}$) on the surfaces of all Au alloys are in good agreement with the original inputs, which is one of the major conditions that has to be fulfilled in the design of multicomponent electrocatalysts.

X-ray diffraction (XRD) was used for the structural characterization of the Au–M/C catalysts. Fig. 2 shows the X-ray diffraction patterns of the various Au–M/C electrocatalysts. As indicated in Fig. 2, the broad peaks (approximately $2\theta = 25^\circ$) are attributed to the (002) plane of the hexagonal structure of Vulcan XC-72R carbon support. All electrocatalysts clearly display five main characteristic peaks of Au face-centered cubic (FCC) crystalline structure, namely, the planes (111), (200), (220), (311) and (222), without peaks of M (Fe, Co, Ni, Cu, Zn). Compared with pure Au, the corresponding diffraction peak positions of Au–M/C are hardly shifted after the addition of M even though the EDS results have verified the existence of M. It is probably because only Au atom crystallizes to form crystal in the Au–M nanoparticles, while M exists in the form of amorphous M atoms adsorbed on the gold crystal [9]. Therefore, the Au–M/C catalysts resemble the single phase disordered structure (interstitial solid solution).

3.2. Voltammeteries of borohydride oxidation on the Au/C and Au–M/C electrodes

The linear voltammograms were recorded at a scan rate of 10 mV s^{-1} as a function of NaBH_4 concentration between 0.01 and 0.2 M for Au/C, Au–Fe/C, Au–Co/C, Au–Ni/C, Au–Cu/C and Au–Zn/C electrodes (Fig. 3). On Au/C (Fig. 3(A)), a wide oxidation wave can be observed between -0.8 and $+0.2 \text{ V}$ versus Ag/AgCl, as the function of BH_4^- concentration since Au is well known for a complete BH_4^- oxidation with a sluggish kinetics [17](Eq. (1)):



Above results also match well with the previously reported BH_4^- voltammograms which are obtained both on a flat Au surface and on Au/C modified glassy carbon electrode [38]. Thus, alloying Au, a fairly inert catalyst for hydrogenation–dehydrogenation processes, with 3d transition metals that not only be widely used for fuel cell catalyst with the unoccupied 3d orbital but also less expensive, such

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