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A detailed study of Au–Ni bimetal synthesized by the phase separation mechanism for the cathode of low-temperature solid oxide fuel cells

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HIGHLIGHTS

- Phase separation mechanism was utilized to save 25% of the noble metal Au.
- A highly active property towards oxygen reduction reactions was achieved.
- Size effect and surface energies differences were used to get nanosphere AuNi.
- A delicate cut and elemental mapping confirmed the core–shell structure of AuNi.
- Morphological and compositional aspects of catalysts were thoroughly investigated.

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ABSTRACT

A facile co-reduction and annealing synthesis route of nanospheric particles of Au–Ni bimetal with adjustable composition was developed. In a typical synthesis, a direct co-reduction of $HAuCl_4.4H_2O$ and $NiCl_2$ in aqueous solution was performed with the assistance of reductive $NaBH_4$ and an anionic surfactant sodium dodecyl sulfate (SDS) functioned as the structure-directing agent. Ultrasonic mixing was used at the same time to control the size of the particles. The morphology, microstructure and the state of the surface atoms were analyzed in detail. These nanospheres showed enhanced electrocatalytic activity towards oxygen reduction reaction than that of pure Au nanoparticles, demonstrated in the low temperature SOFC as cathode. The maximum power density generated is 810 mW cm^{-2} at 550 °C. This is a promising route of taking advantages the Phase Separation Mechanism to greatly reduce the use of noble metals in the ORR field without sacrificing the electrocatalytic activity.

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the favorite power sources amongst various fuel cells due to the diversity of useable fuels such as H_2, formic acid, methanol, ethanol, propyl alcohol, glucose and various hydrocarbons. However, the cost of rare metals or ceramic support, catalyst and the maintenance in high temperature have seriously handicapped their commercialized development. For decades, great efforts have been devoted to lowering the temperature of SOFCs to 550–800 °C, [1–5] where the choice of materials can be expanded and the reliability of cell components will also be improved. In order to reduce the operational temperature without hampering/decreasing the power density, efficient catalysts must be used. Noble metals such as Au, Pd and Pt are the ideal option when only the catalytic activity is taken into account, but the cost is high. There are two ways to deal with this issue.

The first one is to partially replace the noble metal in the catalysts, such as intermetallic compounds, metallic sulfides, metallic oxides, metallic carbides and organometallic compounds; [6–10] The effect of non-noble metal Co, Ni, Biunderlayers/surface impurities on the properties of noble metal overlayers has been successfully utilized towards oxygen reduction for a number of bimetallic systems in the authors former research [11–13]. As is known, nickel represents a unique electrode metal (anodic and cathodic material) of extremely importance for experimental studies and practical industrial applications.

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Nickel is located above the noble metals of Pd and Pt in group VIII of the periodic table and therefore in general behaves similarly to them, and shows similar electrochemical properties. Also, nickel, as a non-noble transition element and due to its availability, plays the role of noble metals for both anodic and cathodic processes in many electrochemical environments. And due to the pronounced passivation features, it shows much higher stability than Co and Fe. It does not rust or suffer from the problems caused by rust.

The second one is to use less amount of noble metal by taking advantage of highly functional nanoparticles. Certain nanoscale morphologies and microstructures are often associated with a perturbation of the outmost layer geometry on an atomic scale [14,15].

In the previous work, the author has tried to improve the properties of the cathode in SOFCs by coating Au nanoparticles onto BICUVOX10($Bi_2Cu_{0.1}V_{0.9}O_{5.35}$), [16] based on previous findings that Au nanoparticles on appropriate carriers can reduce oxygen at low temperatures [17–19]. The Au nanoparticles not only functioned as an electronic network, but also decreased the polarization of the cathodic oxygen reduction reaction. So, in this work, those two ways were combined and Au–Ni binary immiscible systems were prepared with highly organized spherical morphology. The epitaxial constraints stabilizing a homogeneous solid solution on the particles' surface against a phase separation lateral or transverse inhomogeneities were focused in this research. The catalytic activity of the synthesized nanoparticles towards oxygen reduction as the SOFCs cathode was also examined.

2. Experimental section

2.1. Synthesis of the AuNi powders

The chemicals $HAuCl_4.4H_2O$, $NiCl_2$, SDS, HCl and $NaBH_4$ used are all from Alfa Aesar, with purity above 99.9%. In a typical synthesis, 0.1 g of $HAuCl_4.4H_2O$, 0.02 g of $NiCl_2$, 0.25 g of SDS was dissolved in 250 mL of deionized water to form a golden aqueous solution. The pH of the reacting solution was tuned to 4 by HCl addition and then the flask containing the solution was maintained in the bath-type ultrasonicator with a frequency of 100 kHz and temperature of 80 °C. 100 mL of 0.05 M $NaBH_4$ fresh solution was added drop-wise into the flask afterwards. While the reaction took place, the golden solution turned to a bright tartaric color and quickly a black precipitate was obtained on the bottom of the flask. After filtered and washed with deionized water, the powder was dried in an oven at 50 °C. Then the powder was heat-treated at 750 °C in a H_2-Ar atmosphere (H_2 vol. 5%) for 2 h with the increasing temperature rate of 10 °C min^{-1} and decreasing temperature rate of 50 °C min^{-1}. After cooled to room temperature, the powder was washed with 2 M HCl solution and deionized water each for three times and dried in the oven at 50 °C.

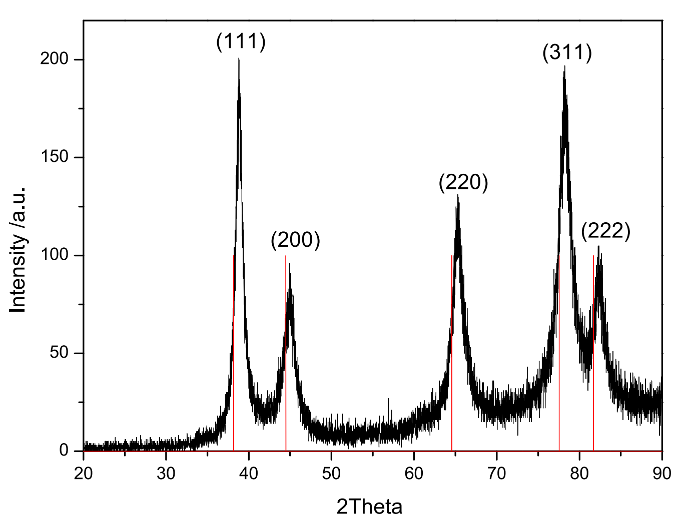

Fig. 1. XRD patterns of $Au_{90}Ni_{10}$.

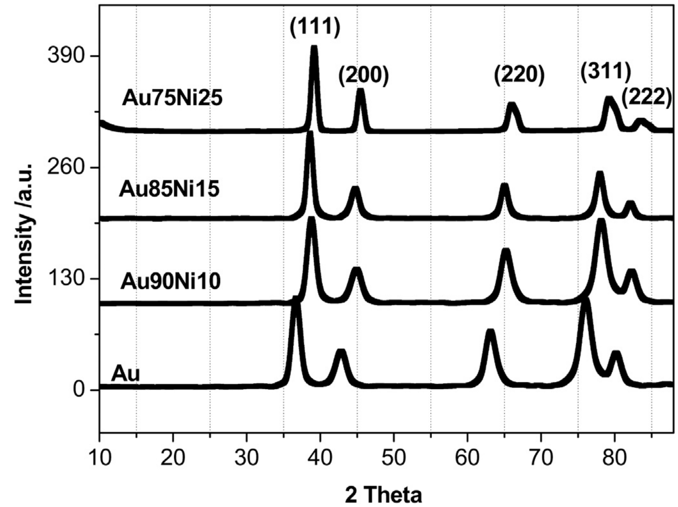

Fig. 2. XRD patterns of Au, $Au_{90}Ni_{10}$, $Au_{85}Ni_{15}$ and $Au_{75}Ni_{25}$.

2.2. Characterization

The samples were characterized by X-ray diffraction by a German Bruker D-8 Advance Diffract Meter with Cu Kα ($\lambda = 1.5405$ Å) radiation. The patterns were recorded between 10 and 80° at increments of 0.02° and counting time of 2s per step. The morphology of the samples was observed in a Jeol JSM-6500F SEM with EDX. The microstructure of the samples was investigated by a Jeol MCL J-2010 Transmission Electron Microscope (TEM) with an accelerating voltage of 200 kV. Before the TEM experiments were performed, the samples were prepared by dispersing a suspension of particles/isopropyl alcohol onto a 3 mm-diameter copper grid

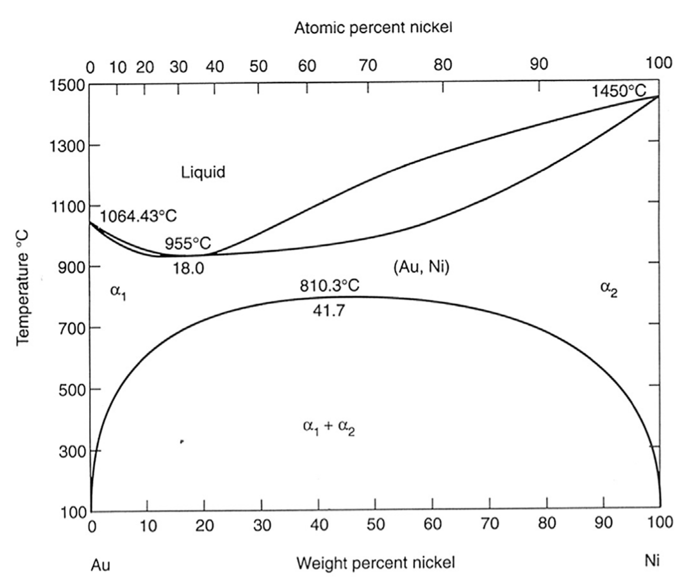

Fig. 3. Phase diagram of Au–Ni.