High Performance Electrocatalysts Based on N-doped Carbon Nanotubes

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Abstract: In this work, the CoFe alloy nanoparticles supported on N-doped carbon nanotubes (CoFe@NCNTs) are synthetized by one-step annealing the precursors without any templates. The as-prepared materials show both extraordinary electrocatalysis activity for ORR and OER in alkaline solution: a diffusion current density of -5.53 mA cm^{-2}, approximate four-electron selectivity as ORR catalyst, a potential of 0.842 V at 10 mA cm^{-2}. Specifically, the CoFe@NCNTs present a Tafel slope of 60.16 mV dec^{-1} as OER catalyst and the variance (ΔE) is below 1.017 V in 0.1 M KOH for the OER and ORR.

Keywords: Electrocatalysts, Doped carbon, CoFe alloy nanoparticles.

1. Introduction

Elecatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is a critical work for developing the fuel cells and the metal-air batteries. Nitrogen-doped carbon and transition metals have been demonstrated as promising catalyst[1-2]. This work reports the synthesis of CoFe alloy nanoparticles supported on N-doped carbon nanotubes (CoFe@NCNTs) by one-step without any templates.

2. Experimental

The CoFe alloy nano-particles are embedded at the tip and uniform located on the graphitic surface of CNTs by one step pyrolysis. Electrochemical measurements were carried out at room temperature on an electrochemical work station (Wavedrive 20 Pine Research Instrumentation) using a standard three-electrode system, with the platinum wire electrode (AFCTR5，≥99.99%, PINE) as the counter electrode and Ag/AgCl double junction reference electrode (saturated gel-KCl ; PINE) as reference electrode, respectively.

3. Results and discussion

The XRD pattern of CoFe@NCNTs indicated that the the CoFe alloy nanoparticles successfully compositing with graphitized carbon. SEM and TEM observation found that the hollow NCNTs cross-linked with each other and the metal nanoparticles are located at the tip and the surface of these tubes. Dark-field STEM elemental mapping showed that these bamboo-like carbon nanotubes are coated by a carbon layer, and we can see clearly that most of CoFe alloy nanoparticles are uniformly located at the tip of the NCNTs.

Electrochemical behavior of the as-prepared electrodes was measured using linear sweep voltammogram (LSV) and cyclic voltammograms (CVs). As depicted in Fig. 1, a CV plot of CoFe@NCNTs can be observed in N_2 and O_2--saturated 0.1 M KOH. There is a positive oxygen reduction peak observed at -0.22 V in O_2-saturated KOH solution, proving that the CoFe@NCNTs have higher ORR catalytic activity. The RDE measurements were also employed to further assess the electrocatalytic activity of CoFe@NCNTs, Fe@NCNTs, Co@NCNTs, and 20% Pt/C in the O_2-saturated 0.1 M KOH solution at 1600rpm. As seen from Fig. 1a, the RDE voltammograms show that CoFe@NCNTs have a more positive onset potential (-0.05 V) and much higher catalytic current density (-5.53 mA cm^{-2}) than other catalysts. Furthermore, the half-wave potential ($E_{1/2}$) of CoFe@NCNTs is 35 mV, which is higher than that of the Pt/C, indicating that CoFe@NCNTs have a superior ORR activity. It can be attributed to the larger specific surface area of the CoFe@NCNTs (307.046 m^2 g^{-1}), which can provide more active sites compared with Fe@NCNTs and Co@NCNTs. Thus structure would benefit the electrochemical properties of the CoFe@NCNTs[3-4].

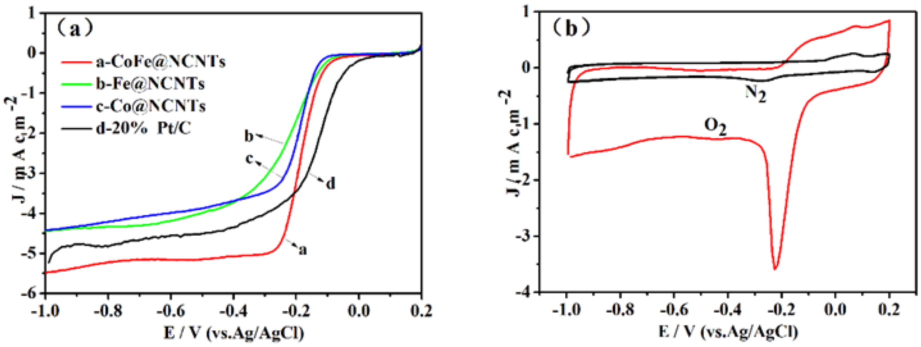

Figure 1. (a) LSVs on rotating disk electrode (RDE) for CoFe@NCNTs, Co@NCNTs, Fe@NCNTs, and Pt/C (20%) at rotation rate of 1600 rpm. (b) Comparison of CV plots of CoFe@NCNTs in N_2- and O_2-saturated in 0.1 M KOH solutions.

To further evaluate the electrocatalytic activity of CoFe@NCNTs for OER, RDE、RRDE measurements were also employed. And the analysis of the electrocatalytic data evidenced that the high activity for the ORR.

4. Conclusions

The CoFe nanoparticles supported on hollow 3D N-doped carbon nanotubes (CoFe@NCNTs) are formed as an efficient bi-functional catalyst in an alkaline solution by one-step pyrolysis. The hollow 3D NCNTs can not only provide more active reaction sites, but it’s thinner carbon walls may accelerate the electron transfer from the metals to the carbon surface, enhance adsorption of O_2 on the surface of NCNTs and then strengthen the ORR and OER activities. In addition, CoFe alloy NPs are embedded at the tip and uniform located on the graphitic surface of NCNTs, which can attribute to the synergistic effect of Fe, Co, and N decoration into NCNTs. And the unique electronic interaction between the CoFe alloy NPs and NCNTs can enhance the catalytic activity and stability of the catalysts. This work provides a facile and effective way to design high-performance non-noble metal catalysts with cheap raw materials, which can be widespread used in rechargeable metal-air batteries, fuel cells, and water splitting.

References

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