Co Nanoparticles Encapsulated in Porous N-Doped Carbon Nanofibers as an Efficient Electrocatalyst for Hydrogen Evolution Reaction

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One of the main challenges in commercializing electrolyzer is to develop cheap and highly active electrocatalysts toward hydrogen evolution reaction (HER). Although low Pt loadings in PEM electrolyzers have been demonstrated, it’s still worthwhile to remove the Pt in the long term. Herein, porous N-doped carbon nanofibers containing encapsulated Co nanoparticles are in situ obtained by electrospinning and subsequent carbonization as efficient electrocatalysts for HER. The optimized catalyst treated at 800 °C shows a remarkably high HER activity with an overpotential of only 159 mV at current density of 10 mA cm−2 in a 0.5 M H2SO4 solution, which is better than most non-precious metal based and metal free catalysts. The carbonization temperature as well as the concentration of nitrogen precursors have significant effects on the structure and catalytic activity of the composites. This work shows the efficacy of preparing noble-metal-free electrocatalysts for HER using the facile electrospinning method.

Journal of The Electrochemical Society, 165 (15) J3271-J3275 (2018)

Manuscript submitted July 26, 2018; revised manuscript received October 11, 2018. Published October 26, 2018. This paper is part of the JES Focus Issue on Electrocatalysis — In Honor of Radoslav Adzic.

Hydrogen is an ideal energy carrier due to its high gravimetric energy density and environmental friendliness. It can be produced by electrolysis of water through hydrogen evolution reaction (HER). Although low Pt loadings in PEM electrolyzers have been demonstrated, it’s still worthwhile to remove the Pt in the long term. Hence, many efforts have been devoted to develop alternative catalysts that are highly active and less expensive. 1, 2 Carbon-based materials with various structures including nanotubes, nanofibers, and nanosheets have been intensively studied. 3–9 They can be supports for metal nanoparticles to reduce aggregation, 10–11 or protective overlayers to avoid the direct contact with the corrosive electrolytes. 12, 13 It has also been proposed that the HER activity of metal particles can be improved by tuning the hydrogen binding energy (HBE) due to the electron redistribution between carbon and metal. 14, 15

Electrospinning has been applied for fabricating continuous carbon nanofibers to encapsulate transition-metal-containing nanoparticles, 16–20 in which the conductive carbon networks can provide efficient electron transport paths while protecting the enclosed nanoparticles from dissolution or detachment. For example, Abouali et al. used electrospun porous carbon nanofibers containing cobalt and cobalt oxide nanoparticles as anode materials for Li-ion batteries. 21 Recently, Shang et al. also found that nitrogen-doped carbon nanofibers with cobalt nanoparticles in them showed good oxygen reduction activity. 20 In this work, we applied the electrospinning technique to prepare porous N-doped carbon nanofibers containing Co nanoparticles. The obtained composite showed excellent HER activity, which was higher than most non-precious metal based and metal free electrocatalysts.

Experimental

Material synthesis.— Polyacrylonitrile (PAN, Mw = 150,000 Aldrich) and cobalt (III) acetylacetonate (Aldrich) were chosen as the carbon and Co precursors, respectively. N,N-dimethylformamide (DMF, Aldrich) was used as the solvent. First, 0.5 g PAN was added into 10 ml DMF and stirred in a water bath at 90 °C for 2 h to form a homogenous solution with a PAN concentration of 5%. Then 0.21 g cobalt (III) acetylacetonate was added into the solution and stirred for 1 h. The as-prepared precursor solution was transferred into a 20 ml syringe with a 18G needle (outer diameter = 1.2 mm). A high voltage of 16 kV of an electrospinning unit (KATO Tech. Co., Japan) was applied between the needle and rotation collector placed at a constant distance of 18 cm with a flow rate of 1.0 ml h−1. The electrospun composite was collected on an aluminum foil. It was then dried and peeled off from the collector. The composite was stabilized at 220 °C for 3 h in air and then carbonized at 800 °C for another 1 h in argon with a heating rate of 5 °C min−1 in a tube furnace (NBD-O1200-501T, Nobody). The final product was named Co-PAN(5%)-800. For comparison, PAN nanofiber was also prepared in the same way without adding cobalt precursor. The effects of the carbonization temperature (700 °C, 800 °C, and 900 °C) and PAN concentration in DMF solution (vol. 4%, 5%, and 7%) on the structure and HER activity of the final products were systematically investigated.

Characterization.— All the characterizations were done in the Materials Characterization and Preparation Facility (MCPF) at the HKUST. Crystal structures of materials were examined by a Philips PW1830 powder X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å) and a graphite monochromator. The applied current and voltage were 20 mA and 40 kV, respectively. The scanning range of 20 varied from 10 to 80° at a detector angular speed of 2 ° 0 min−1 and the step size was 0.02°. The obtained spectra were analyzed against the patterns from the International Center for Diffraction Data (ICDD). The morphologies were recorded using a scanning electron microscopy (SEM, JEOl 7100) and transmission electron microscopy (TEM, JEM 2010). The elemental composition and chemical state of the samples were measured by X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra DLD multi-technique surface analysis system. Thermogravimetric analysis (TGA) was conducted (TGA Q5000 testing system) with a temperature range from room temperature to 800 °C with a heating rate of 5 °C min−1 in air.
Electrochemical tests.—The electrochemical measurements were carried out in a traditional three-electrode cell controlled by a CH Instruments electrochemical workstation (627E). The prepared samples were grind into powder firstly. 5 mg of sample and 10 μL of Nafion solution (5%, Aldrich) were dispersed in 1 mL water solution containing 0.2 ml of isopropanol. The mixture was sonicated for 30 min to form a well-dispersed ink. Then 30 μl of the ink was added onto a glassy carbon electrode (surface area = 0.196 cm²) to form a uniform thin catalyst film as the working electrode. The mass loading of the catalyst on the working electrode was 0.765 mg cm⁻². The Ag/AgCl (saturated with KCl) and Hg/HgO (saturated with KOH) electrodes were used as the reference electrodes in acidic and alkaline solutions, respectively. To avoid possible contaminations from counter electrode, a carbon rod (6 mm diameter) was used as the counter electrode in all electrochemical measurements. All potentials were calibrated to a carbon rod (6 mm diameter) was used as the counter electrode in all electrochemical measurements. All potentials were calibrated to a reversible hydrogen electrode (RHE). Before HER activity measurements, the thin film electrode was firstly cycled in an Ar-saturated 0.1 M HClO₄ solution (Aladdin, 99.999%) or 1.0 M KOH (Aladdin, 99.99%) solution between 0.05 and 1.2 V for 10 cycles at 100 mV s⁻¹. After that, the electrode was then transferred to another electrochemical cell containing Ar-saturated 0.5 M H₂SO₄ or 1.0 M KOH solutions to measure the HER activity. Linear sweep voltammetry (LSV) was conducted with a scan rate of 10 mV s⁻¹ from 0.1 V.

Results and Discussion

A typical SEM image of Co-PAN(5%)-800 nanofibers is shown in Figure 1a. The bead-free nanofibers have diameters in the range of 100–200 nm. When compared with the pristine Co-PAN(5%) nanofibers without heat-treatment (Figure S1a) and the one stabilized at 220 °C in air for 3 h (Figure S1b), the Co-PAN(5%)-800 nanofibers maintained the original fiber morphology after carbonization. The TEM image (Figure 1b) shows uniform distribution of nanoparticles with an average particle size of ~9 nm in porous carbon nanofibers after carbonization (pores are pointed out in Figure 1b). The high-resolution TEM image in Figure 1c demonstrates that the particle was well encapsulated by graphitic carbon layers. The interplanar distance of 0.36 nm corresponds well to the (002) plane of crystalline graphite. These particles were confirmed to be Co by the energy-dispersive X-ray spectroscopy (EDS) shown in Figure 1d. Figure 1f indicates that N was uniformly distributed in the carbon nanofiber. To achieve an optimized carbonization temperature that gives rise to balanced morphology and electrocatalytic performance of composites, the stabilized Co-PAN(5%) nanofibers were carbonized at different temperatures (700 °C to 900 °C) and their SEM and TEM images are shown in Figure S2. When pyrolyzed at 700 °C, both Co-PAN(5%)-700 and Co-PAN(5%)-800 share essentially a similar structure, as shown in Figure S2a. However, the former nanofibers contain fewer Co nanoparticles and look solid with no visible pores (Figure S2b). When the carbonization temperature was raised to 900 °C, the surfaces of nanofibers became rougher (Figure S2c) with much larger Co nanoparticles (30–50 nm) and larger internal pores (Figure S2d) than the counterparts carbonized at lower temperatures. The formation of pores is known to be driven by dehydration from the Co precursor as well as evaporation of volatile and non-carbon elements in the PAN matrix. Therefore, the carbonization temperature appears to have played an important role in the formation of both Co particles and pores.

To further investigate the structure of prepared materials, XRD patterns of Co-PAN(5%) calcined at different temperatures were collected and shown in Figure 2. All samples showed a broad peak at ~24° corresponding to the (002) plane of graphite. Co-PAN(5%)-800 and Co-PAN(5%)-900-800 both exhibited three clear peaks at around 44°, 56° and 76° that were attributed to the (111), (200) and (220) planes of Co (JCPDS 15-0806), respectively. According to the Scherrer equation, the average particle size is \( \tau = \frac{4\lambda}{\beta\cos\theta} \), where \( \lambda \) is the X-ray wavelength, \( \beta \) is the peak width at half maximum height and \( K \) is a constant related to crystallite shape. The particle sizes calculated from the (111) peak were 8.2 nm and 13.2 nm for the 800 °C and 900 °C samples, respectively. This indicated that higher temperatures can promote the formation of larger Co particles. For Co-PAN(5%)-700, the peaks associated with Co particles were very weak due to the smaller particle size of Co, which is consistent with the TEM characterization results (Figure S2).

Next, the effect of PAN concentration in DMF (vol. 4%, 5%, and 7%) was investigated for the samples treated at 800 °C. The SEM and
TEM images of Co-PAN(7%)-800 and Co-PAN(4%)-800 are shown in Figure S3. The Co-PAN(7%)-800 (Figure S3a) also showed a bead-free nanofiber structure which was similar with Co-PAN(5%)-800 but without pores. The diameter of Co-PAN(7%)-800 was larger (200-400 nm), while the particle size of Co was smaller and many tiny particles appeared near the surfaces of the nanofibers (Figure S3b). Accordingly, the peaks in the Co XRD patterns of Co-PAN(7%)-800 were broader (Figure S4). When the PAN concentration is high, the content of Co precursor in the solution is relatively lower resulting in the formation of smaller Co particles during heat-treatment. When the concentration of PAN was decreased to 4%, the pristine nanofibers looked much the same as other fibers which remained even after stabilization at 220 °C (the inset of Figure S3c). After carbonization at 800 °C, however, they were broken into short porous rods with Co nanoparticles encapsulated in them (Figure S3d). The size of Co particles was similar with that of Co-PAN(5%)-800 as confirmed by TEM and XRD (Figure S4).

To quantify the contents of Co in these three samples, TGA was conducted from room temperature to 800 °C in the air with the heat rate of 5 °C min⁻¹ (Figure S5). For all three samples, they showed a similar trend with a weight decrease starting from around 250 °C and then a sharp weight loss at 330 °C-370 °C. A plateau was reached after ~450 °C where the final product was Co₃O₄. Co-PAN(7%)-800 showed a slightly delayed weight loss at a higher temperature than the other two probably due to a longer time required to evaporate volatile materials. The Co contents according to the TGA curves were 4.6, 4.0 and 2.5 wt%, respectively, for those containing 4, 5 and 7% PAN, as summarized in Table S1. As expected, the higher the PAN concentration, the lower the weight percentage of Co. Therefore, a high PAN concentration produced the nanofibers with larger diameters and better thermal stability, which might be caused by a smaller amount of Co nanoparticles in fibers since they act as a catalyst to the gasification of carbon. If the PAN concentration was too low, the carbon nanofibers were easily broken to form nanorods during carbonization.

The elemental composition of Co-PAN was further analyzed by XPS. The general survey spectra for samples treated at different temperatures are shown in Figure S6. Several peaks for C 1s, N 1s, O 1s and Co 2p can be clearly identified. It was noticed that when the carbonization temperature increased, the peak intensity of N 1s decreased suggesting a decrease of nitrogen content. Its contents are 9.1%, 5.3%, and 3.3% for the 700 °C, 800 °C, and 900 °C heated samples, respectively, as summarized in Table S2. The detailed scan in the N 1s region is shown in Figure 3a for Co-PAN(5%)-800 and Figure S7 for Co-PAN(5%)-700 and Co-PAN(5%)-900. The N1s signal can be deconvoluted into different groups including pyridinic N (398.1 eV), pyrrole N (400.5 eV), graphitic N (401.7 eV) and oxidized N (403.7 eV). According to the peak intensity, pyridinic and pyrrole N accounted for a large proportion of the total N for all three samples (Figure 3d). It is inferred that pyridinic and pyrrole N might be closely related to their catalytic activities. The C 1s spectra were deconvoluted into C-C (284.5 eV), C-N (285.7 eV) and O-C=O bonds (288.4 eV) (Figure 3b and Figure S7). All samples showed similar C 1s spectra and C-C takes up the largest percentage of total C. In terms of the high-resolution signal of Co 2p in Co-PAN(5%)-800 (Figure 3c), the peak can be deconvoluted into metallic Co (786.6 eV) satellite, respectively. Co mainly existed in its metallic form which is consistent with the EDS mapping and XRD results.

The electrochemical performance of prepared Co-PAN nanofibers was evaluated using a thin film glassy carbon electrode in a liquid cell with a catalyst loading of 0.765 mg cm⁻². The thin film electrode was firstly cycled in an Ar-saturated 0.1 M HClO₄ solution between 0.05 and 1.2 V for 10 cycles at 100 mV s⁻¹ for cleaning. Figure 4a shows a typical CV curve of Co-PAN(5%)-800 in an Ar-saturated 0.1 M HClO₄ solution. No obvious oxidation peak was observed up to 1.2 V. For comparison, we also prepared PAN nanofibers following the same procedure without adding Co precursor. PAN nanofibers showed solid structure without pores as shown in Figure S8. This also implies that the porous structure was generated by the decomposition of Co precursors. The current density of CV curve of PAN was much smaller than that of Co-PAN(5%)-800. This might because of the absence of Co nanoparticles in PAN as well as low specific surface area due to the solid structure. The HER activities of Co-PAN nanofibers were investigated using the LSV by sweeping the potential from 0.1 V to negative potentials in a 0.5 M H₂SO₄ solution with a scan rate of 10 mV s⁻¹. The polarization curves for Co-PAN(5%) at different carbonization temperatures (700 °C, 800 °C, and 900 °C) after ir-compensation and background correction are shown in Figure 4b. Their overpotentials (η) at current density of 10 mA cm⁻² increased following the trend of 800 °C, 900 °C and 700 °C. Co-PAN(5%)-800...
had the highest activity for HER, with a small overpotential of 159 mV at current density of 10 mA cm$^{-2}$. The activity was much better than the sample derived from PAN without metal precursor, which showed an overpotential of 408 mV. This demonstrated the important role of Co in improving the HER activity of the composite. Co-PAN(5%)-700 exhibited a catalytic activity with an overpotential of 370 mV at current density of 10 mA cm$^{-2}$. This was much worse than the other two samples. The activity of Co-PAN(5%)-800 in acid with a loading of 0.765 mg cm$^{-2}$ was better than most non-precious-metal-based and metal free catalysts for HER.26–31 Figure 4c shows the comparison between the polarization curves of Co-PAN-800 with different PAN concentrations (4%, 5%, 7%) in an Ar-saturated 0.5 M H$_2$SO$_4$ solution. Their overpotentials at current density of 10 mA cm$^{-2}$ were 190 mV, 159 mV, and 366 mV, respectively. Co-PAN(7%)-800 showed a much worse catalytic activity than other two samples. We further investigated the effect of Co content in the composite. The amount of Co precursor was doubled to 0.42 g with other conditions fixed. The sample was marked as Co-PAN(5%)-800. The results indicated that further increasing the Co content would lead to a worse HER activity as shown in Figure S9. This was probably due to the aggregation of Co particles with a relatively high Co content in the precursor solution. To understand the performance of these catalysts at different pH, we also tested the HER activity of Co-PAN(5%)-800 in a 1.0 M KOH solution. CV curves were recorded in an Ar-saturated 1.0 M KOH solution. Their overpotentials at current density of 10 mA cm$^{-2}$ were 70 mV, 60 mV, and 220 mV, respectively. Co-PAN(7%)-800 showed a very low overpotential of 159 mV at the current density of 10 mA cm$^{-2}$ in a 0.5 M H$_2$SO$_4$ solution, which was better than most non-precious-metal-based and metal free catalysts. According to our results, the carbonization temperature as well as the PAN concentration in DMF have significant effects on the morphology and catalytic activity of the composites. This work shows the efficacy of preparing the noble-metal-free electrocatalysts for HER using the electrospinning method.

Acknowledgment

The authors acknowledge the start-up fund from the Hong Kong University of Science and Technology, the Research Grant Council (N_HKUST610/17) of the Hong Kong Special Administrative Region, Guangdong Special Fund for Science and Technology Development (Hong Kong Technology Cooperation Funding Scheme 201704030019 and 201704030065).

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Conclusions

In this work, we demonstrated that porous N-doped carbon nanofibers containing encapsulated Co nanoparticles obtained by electrospinning and subsequent carbonization have a good activity for HER, especially in acidic solutions. The optimal catalyst Co-PAN(5%)-800 showed a very low overpotential of 159 mV at the current density of 10 mA cm$^{-2}$ in a 0.5 M H$_2$SO$_4$ solution, which was better than most non-precious-metal-based and metal free catalysts. According to our results, the carbonization temperature as well as the
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