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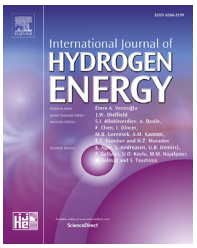

Taming transition metals on N-doped CNTs by a one-pot method for efficient oxygen reduction reaction

Yuying Gao [a], Li Wang [a,b], Guozhu Li [a,b,*], Zhourong Xiao [a], Qingfa Wang [a,b], Xiangwen Zhang [a,b]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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ABSTRACT

Various transition metals have been incorporated into nitrogen-doped carbon nanotubes (M-N-C/CNT, M = Fe, Co, Mn, and Ni) via a one-pot method using dopamine as nitrogen source and metal salts as precursors for oxygen reduction reaction (ORR). Raman spectra and XRD patterns of the catalysts were collected to characterize the graphitization degree and metal state. XPS was employed to determine atom state and element fraction. The electrochemical performance of the catalysts for ORR were evaluated in alkaline media at −0.8 V to 0.2 V. The E_{onset} and $E_{1/2}$ with the values of −100 mV and −170 mV (vs Ag/AgCl) are achieved on Mn-N-C/CNT-800. The superior selectivity toward the $4e^-$ pathway are obtained on Mn-N-C/CNT-800 and Co-N-C/CNT-800 with the transferred electron numbers per O_2 molecule of 4.12 and 3.94, respectively. Results show that the states of doped transition metal play a key role on determining ORR performance. The electron transfer number of Ni-N-C/CNT at −0.5 V is increased from 3.22 (Ni-N-C/CNT-800) to 3.99 (Ni-N-C/CNT-600) when the metallic Ni has been eliminated at lower pyrolysis temperature.

Introduction

Fuel cells and air-batteries are high-efficiency energy conversion and storage devices, in which oxygen reduction reaction (ORR) is a crucial process [1–4]. Although the conventional Pt-based electrocatalysts are commonly used, its high-cost and susceptibility have prompted the extensive research for alternative low-cost and high-performance ORR electrocatalysts [3,5,6].

The heteroatom-doped carbon catalysts are found to be superior to Pt for ORR without CO deactivation and fuel crossover effects in alkaline medium. Tuning properties of carbon materials by doping heteroatoms, such as N [7–18], S [7,19–24], B [25,26] and P [27], has been reported. Some earth-abundant materials having similar surface electronic properties to Pt such as M_xO_y (M = Fe, Co, etc.) [28,29], M_xN_y (M = Mo, Co, Ti, Ta, etc.) [30]' and M_xS_y (M = Co, Fe, Ni, etc.) [31–33] are also considered as alternatives. However, the metal-free carbon nanomaterials or metal materials usually

* Corresponding author. Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.
E-mail address: gzli@tju.edu.cn (G. Li).

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possess relatively limited electrocatalytic ability toward ORR [34].

Recently, the design and synthesis of metal-nitrogen-carbon (M-N-C) type (commonly, Fe and Co) electrocatalysts for ORR have attracted considerable interest due to their better durability and stronger tolerance against methanol crossover. Fe_2N/mesoporous nitrogen-doped graphitic carbon spheres (MNGCS) catalysts were prepared by Xiao et al. and the optimal one showed high ORR activity and good durability in alkaline media compared with 10 wt% Pt/C [35]. Hollow carbon nanospheres catalyst co-doped with N and Fe-containing species exhibited high ORR activity comparable to the commercial 20 wt% Pt/C catalyst [36]. Li et al. synthesized M/N-C hybrids (M = Fe, Co, and Ni) using the robust approach and found that Co/N-C exhibited higher stability and catalytic activities towards ORR than others [37]. Chen et al. realized a remarkable ORR performance by designing unique hollow structure with large surface areas of hollow porous carbon spheres with Co nanoparticles and nitrogen co-doped (Co-HNCS) [38].

In this work, the effects of transition metal on the performance of M-N-C/CNT (M = Co, Mn, Ni and Fe) catalysts will be investigated. Firstly, M-N-C/CNT catalysts are prepared via one-pot method with dopamine as nitrogen source and transition metal salts as precursors. Secondly, the structures and properties are characterized by XRD, Raman, TEM, XPS techniques and N_2 adsorption/desorption instrument. Finally, cyclic voltammetry (CV) curves and linear sweep voltammetry (LSV) curves are measured by RDE technique in the KOH solution to evaluate the performance of electrocatalysts.

Experimental

Materials

Dopamine hydrochloride (DA·HCl, 98%), Tris(hydroxymethyl) aminomethane (Tris), potassium chlorde (KCl, 99.99%) and potassium hydroxide (KOH, 95%) were purchased from Aladdin Co. Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%) was purchased from Shuangchuan Co., Tianjin. Manganese (II) acetate ($Mn(CH_3COO)_2$, 98%) was purchased from Meryer Co., Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%) was purchased from Fuchen Co., Tianjin. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 98%), ethanol (99.7%) and methanol (99%) were purchased from Guangfu Co., Tianjin. Isopropyl alcohol (99.7%) was purchased from Huadong Chemicals Co., Tianjin. Nafion (5 wt%) was purchased from Alfa Aesar Co. Ultra-purity water (UP water, 18.2 MΩ) was from Milli-Q UV (Millipore) water system. Multi-walled carbon nanotubes (MWCNTs, OD = 10–20 nm, Length = 10–30 μm) were purchased from Timesnano Co., Sichuan.

Synthesis of M-N-C/CNT catalysts

The synthetic procedure of M-N-C/CNT catalysts is shown in Scheme 1. 0.2 g DA·HCl and certain amount of metal salt (molar ratio of M^{n+} to DA was 1:1, $M^{n+} = Fe^{3+}$, Co^{2+}, Ni^{2+}, Mn^{2+}) were added into 500 mL deionized water, forming M-DA complex. 0.3 g CNTs were added into the mixture and stirred at room temperature for 0.5 h. Then certain amount of Tris was added into the suspension, keeping pH at 8.5. The suspension thus obtained was stirred at room temperature for 24 h. Finally, the suspension was centrifuged, washed with deionized water for three times and ethanol for once, and dried in vacuum, yielding M-PDA-CNT.

M-PDA-CNT was pyrolyzed in a tube furnace under N_2 atmosphere at 800 °C for 2 h with a heating rate of 5 °C min^{-1}. The as-prepared catalysts are denoted as M-N-C/CNT-800 (M = Co, Mn, Ni, and Fe) where 800 represents pyrolysis temperature. For a comparison study, N-C/CNT-800 was prepared by the same procedure and conditions without adding metal salt.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE powder X-ray diffractometer, using Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA). XRD patterns were collected among 2θ = 10°–80° and at scan rate of 5°/min. Raman characterization was carried out using a DXR Raman microscope (Thermo Fisher Scientific) with a 532 nm-wavelength laser. The morphology and structure of the samples were measured using a transmission electron microscope (TEM, Tecnai G2 F20, USA) operating at an acceleration voltage of 200 kV. N_2 adsorption/desorption measurements were carried out using a volumetric adsorption analyzer (Autosorb-iQ, Quantachrome Instruments US) at 77 K. X-ray photoelectron spectroscopy (XPS) measurement was conducted on Thermo ESCALAB 250XI with a monochromatized Al Kα X-ray source (1486.6 eV photons).

Electrochemical measurements

Working electrode preparation

A glassy carbon electrode (GCE, 5 mm in diameter, geometric area = 0.196 cm^2) was polished with 1 μm, 0.5 μm and 0.05 μm alumina powder slurry, respectively, and then ultrasonicated several times in ethanol and deionized water to get a mirror-like surface. 3 mg as-prepared catalyst was dispersed in a mixture containing 750 μL deionized water and 250 μL isopropyl alcohol and then ultrasonicated for 30 min. Then 25 μL Nafion solution was added into the mixture and ultrasonicated for at least 2 h to form a homogeneous ink. 15 μL catalyst ink was coated on the surface of the GCE and then dried at room temperature to form a catalyst film. The catalyst loading on GCE was 0.229 mg cm^{-2}.

Electrochemical measurement

All electrochemical measurements were performed on CompactStat.h10800 potentiostat/galvanostat/electrochemical analyzer (Ivium Technologies co., Netherland), equipped with a rotation speed controller (Pine Instrument co., USA). The measurements were conducted in a three-electrode system. Gauze-Pt (1 cm × 1 cm) was employed as the counter electrode, Ag/AgCl (saturated KCl solution) was used as the reference electrode, and the catalyst-coated GCE was served as the working electrode, respectively.

Cyclic voltammetry (CV) curves were collected in 0.1 M O_2-saturated KOH solution at a scan rate of 10 mV s^{-1} from 0.2 V

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