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Significantly enhanced oxygen reduction activity of Cu/CuN$_x$C$_y$ co-decorated ketjenblack catalyst for Al–air batteries

Fuzhi Li [a,b], Jingsha Li [a], Qiuju Feng [c], Jun Yan [a], Yougen Tang [a,d,*], Haiyan Wang [a,d,*]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China
[b] College of Life Sciences and Chemistry, Hunan University of Technology, Zhuzhou 412008, Hunan, China
[c] College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, Hunan, China
[d] Hunan Provincial Key Laboratory of Efficient and Clean Utilization of Manganese Resources, Central South University, Changsha 410083, Hunan, China

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ABSTRACT

Highly efficient and non-precious catalysts are imperative for oxygen reduction reaction (ORR) to replace Pt/C. Anchoring efficient active species to carbon supports is a promising and scalable strategy. Here we synthesize Cu nanoparticles and noncrystalline CuN$_x$C$_y$ species co-decorated ketjenblack (KB) carbon catalyst (denoted as Cu-N-KB-acid) by a facile and scalable method using copper sulfate, melamine, and KB as raw materials. An initial one-pot hydrothermal treatment is designed before pyrolysis process to achieve the good distribution of Cu and melamine on KB via a possible chelation effect. Owing to the synergistic effect of Cu and CuN$_x$C$_y$ on KB, this composite catalyst displays excellent ORR catalytic activity in alkaline solution, which is comparable to the commercial 20% Pt/C. When used as a catalyst in a home-made Al–air battery, it shows a stable discharge voltage of 1.47 V at a discharge density of 50 mA cm^{-2}, a little higher than that of Pt/C (1.45 V).

1. Introduction

Owing to the sluggish reaction kinetics, oxygen reduction reaction (ORR) is considered as the major bottleneck for developing advanced metal air batteries [1–6]. To address such issue, Pt-based catalysts are widely used as the state-of-the-art catalyst. However, their rare reserve, high price and sensitivity to CO poisoning have inspired lots of researches to pursue low cost and highly efficient candidate to replace the commercial Pt/C catalyst. Among these catalysts, carbon materials functionalized with nitrogen [7–9] or transition metals and nitrogen (marked as TM-N-C or TMNC, where TM = Fe, Co, Cu, etc., N = nitrogen, C = carbon) have been reported as two competitive classes of non-precious catalysts for the ORR [10–12]. Fe-N-C catalysts have attracted particular attention owing to their comparable ORR catalytic activity to commercial Pt/C [11,13–17]. Although the nature of the active sites in TM-N-C composite still remains controversial, it is well accepted that both the non-crystalline TMN$_x$C$_y$ moieties and the crystalline metal-based nanoparticles (e.g. M, M$_3$C, where M = metal) encased in the surrounding graphitic carbon layers are proposed as the main active sites [18].

Recently, the copper-based catalysts have attracted much attention because of their low overpotential for O$_2$ reduction to H$_2$O [3,19], high electronic conductivity (just less than Ag), low price and relatively large abundance [8]. Cho et al. [20] developed nano-CuS@Cu-BTC (BTC = 1,3,5-benzenetricarboxylate) composite using Cu-BTC and thioacetamide as raw materials, which exhibited an onset potential of 0.91 V (vs. RHE, reversible hydrogen electrode) and quasi-four-electron transfer pathway ($n = 3.82$). Periasamy et al. [21] prepared Cu$_9$S$_8$/CNTs nanocomposites with an onset potential of −0.18 V (vs. SCE, saturated calomel electrode) and a near four-electron pathway in alkaline media for ORR. Wu et al. [19] prepared Cu-N@C catalyst utilizing copper phthalocyanine (CuPc) and dicyandiamide, and found that the highly exposed Cu(I)–N active sites greatly promoted the ORR catalytic activity. Cu, N-co-doped carbons (Cu–N–C) derived from Cu-containing ZIF-8 also exhibited good performance for ORR due to the Cu, N-doping and porous structure [8]. A highly efficient copper-containing catalyst was synthesized by embedding 5-nitrophenanthroline into polyvinylimidazole (PVI), which wrapped around the carbon nanotubes [3]. Although these copper based catalysts showed good catalytic activity for ORR, the preparation process often involved expensive materials such as CuPc [19], ZIF-8 [8], CNT [21], BTC [20], 5-nitrophenanthroline and PVI (polyvinylimidazole) [3]. Therefore, it is indispensable to improve the catalytic performance with cheap raw materials as much as possible. Nitrogen doping is an essential

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[*] Corresponding authors at: College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China.
E-mail addresses: ygtang@csu.edu.cn (Y. Tang), wanghy419@126.com (H. Wang).

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step in the preparation of TM-N-Cs for ORR. In general, nitrogen doping was gained by the pyrolysis of nitrogen-containing precursors, such as melamine [22–24], 1-octadecylamine [25], cyanamide, dicyandiamide and polyaniline [18,26–28]. These precursors generally generate a great deal of gases during pyrolysis. When these gases flow out, they take samples away and lead to a relatively low yield.

In this work, we introduced a facile and scalable way to synthesize Cu and CuN_xC_y co-decorated ketjenblack (KB) composite (denoted as Cu-N-KB-acid) using low cost materials such as copper sulfate, melamine and KB. Hydrothermal process was first employed before the pyrolyzation to achieve better distribution of the doped Cu and N. In the meantime, the pyrolyzation process was optimized by wrapping the porcelain boat with copper foil, resulting in much higher yield (~32.32% for wrapped and ~5.01% for unwrapped). Owing to the interaction of CuN_xC_y, Cu nanoparticles and KB supports, the as-prepared Cu-N-KB-acid exhibited significantly improved ORR activity in 0.1 M KOH solution, which is comparable to the commercial Pt/C (Johnson Matthey, 20 wt%). When used in home-made Al–air batteries, it also showed a little higher practical discharge voltage.

2. Experimental

2.1. Preparation of catalysts

All chemical reagents used in this work are of analytical grade and without further purification. First, 0.2 g of KB was added into a homogenous aqueous solution containing 1.0 g of copper sulfate, then magnetically stirred at least for 10 min. Second, 1.1 g of melamine was added into the mixed solution, then stirred for 30 min. Third, the resulting solution was enclosed into a 100 mL Teflon lined stainless steel shell autoclave, heated to 120 °C in an oven and kept at the temperature for 24 h. After it was cooled to room temperature naturally, the as obtained product was filtrated under vacuum with membrane of 0.15 µm pore diameter and dried overnight at 80 °C. After carefully ground by agate mortar for more than 5 min, the resulting powder was transferred to a piece of porcelain boat, which was then covered with another piece of porcelain boat and further wrapped by copper foil. The treated porcelain boat was placed into a tube furnace and then heated to 650 °C for 2 h at a heating rate of 5 °C min^{-1} in argon flow. After that, it was naturally cooled to room temperature. Finally, the obtained sample was treated with 3 M HCl at 80 °C for 6 h with continuous agitation to remove unstable phases [1,12]. After filtration, washing and drying, the collected sample was heated again at 650 °C for 1 h to repair the catalyst surface and reinforce the grain phases [29,30]. The as prepared catalyst was denoted as Cu-N-KB-acid. For comparison, the sample without acid treatment was denoted as Cu-N-KB.

We also synthesized three control samples, N-KB, Cu-N and Cu-KB. For N-KB, all procedures were the same with Cu-N-KB but without the addition of copper sulfate. For Cu-N, all procedures were the same with Cu-N-KB but no KB was added. For Cu-KB, all procedures were the same with Cu-N-KB but no melamine was added. It should be noted that no acid treatment and no subsequent pyrolysis procedure were employed for these control samples.

2.2. Physical characterization of catalysts

X-ray diffractometer (Rigaku D/Max 2550) was used to characterize the structures of the as-prepared samples. The morphologies and microstructures of these catalysts were studied using transmission electron microscopy (TEM, Titan G2 60-300). X-ray photoelectron spectroscopy (XPS) test was detected on K-Alpha1063 spectrometer. Nitrogen adsorption/desorption isotherms were recorded using Quantachrome autosorb-1. The Raman spectrum was tested by Raman Spectrophotometer (Labram-010, $\lambda_{ex} = 632$ nm).

2.3. Electrochemical measurements

For electrochemical measurements, 6 mg of as-prepared catalyst was dispersed in 950 μL anhydrous ethanol by sonication for 20 min, then 50 μL of nafion solution (5 wt%) was added and sonicated for another 20 min to get a homogeneous catalytic ink. 10 μL of the ink was loaded onto the surface of glassy carbon disk, and the catalyst loading is 0.2437 mg cm^{-2}. For comparison, the commercial 20 wt% Pt/C (Johnson Matthey) was also prepared with the same method.

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed using a double fluid boundary Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode in 0.1 M KOH solution saturated with oxygen on a CHI760E electrochemical workstation. All potentials were finally converted to the values versus reversible hydrogen electrode.

The Koutecky–Levich equation was used for the electron transfer number (n) calculation, the detailed formula can be obtained in references [1,31]. To further verify the ORR mechanism, the peroxide percentage and the number were calculated based on the equations in references [1,31]. The kinetic current for Tafel plot was calculated according to the equation shown in reference [1].

2.4. Electrochemical test of Al–air batteries

For Al–air full batteries test, a polished aluminum stripe was used as anode, a 6 mol L^{-1} KOH solution containing 0.01 mol L^{-1} Na_2SnO_3, 0.0075 mol L^{-1} ZnO and 0.0005 mol L^{-1} $In(OH)_3$ was used as electrolyte. The air electrodes were composed of gas diffusion layer, foam nickel current collector and catalytic layer. The catalytic layer was fabricated as follows. The as-prepared catalysts (60 mg) and the 60 wt% polytetrafluoroethylene (PTFE) aqueous solution (50 mg) were mixed and agitated continuously until a paste appeared, and then rolled with glass rod until it turned into a film with the size of 2 × 2 cm. In the end, the film and gas diffusion layer were pressed onto the two sides of nickel foam under the pressure of 15 MPa, and dried at 60 °C for overnight. For comparison, the air electrode using commercial 20 wt% Pt/C catalyst was also fabricated with the same method. The full battery performance was measured with Neware battery testing system (Shenzhen, China). A home-made electrochemical cell was used for Al–air battery measurements, with the net volume size of 50 × 32 × 50 mm and a 10 mm diameter air hole was used for the test. Other details can be seen in our previous references [2,31,32].

3. Results and discussion

Fig. 1(a) shows the XRD patterns of Cu-N-KB-acid, Cu-KB and N-KB. Fig. 1(b) shows the XRD patterns of Cu-N-KB, Cu-N and the PDF cards. As shown in Fig. 1(b), Cu-N-KB catalyst shows a broad diffraction peak at about 26°, which is assigned to carbon (0 0 2) [19,33]. There are two other phases existing in Cu-N-KB, Cu and Cu_2S. The sharp peaks at 43.3°, 50.45°, 74.1° are well indexed to metallic Cu (PDF#97-006-4699), demonstrating that a certain amount of Cu^{2+} was efficiently reduced to Cu during the synthesis process. The weak peaks at 32.64°, 37.4°, 39.05°, 45.9°, 48.4° can be indexed to the chalcocite Cu_2S (PDF#97-002-3596). For the pattern of Cu-N-KB-acid in Fig. 1(a), no obvious peaks of Cu phase and Cu_2S phase are observed except the broad diffraction peak of

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