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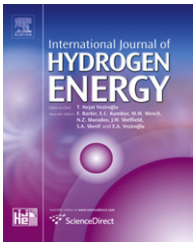

Nitrogen-doped carbon xerogel as high active oxygen reduction catalyst for direct methanol alkaline fuel cell

Sisi Liu [a,b], Huamin Zhang [a,*], Zhuang Xu [a,b], Hexiang Zhong [a,**], Hong Jin [b,c]

[a] Division of Energy Storage, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China
[c] Department of Engineering, Shenyang Agricultural University, Shenyang 110866, China

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ABSTRACT

A novel catalyst based on nitrogen-doped carbon xerogel for oxygen reduction reaction (ORR) was prepared via a sol–gel process, following by the subsequent pyrolysis under ammonia atmosphere. The catalytic activity in alkaline media was optimized by tuning the metal (cobalt) ratio to the gel precursor. Sample with the optimum activity was characterized by transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis and electrochemical measurements. Results show that the catalyst possesses an amorphous microstructure with nitrogen doped on the surface. The nitrogen-doped carbon xerogel displays comparable ORR activity and superior methanol tolerance than Pt/C in alkaline medium, demonstrating its promising application in direct methanol alkaline fuel cells as non-precious cathode catalyst.

1. Introduction

The direct methanol fuel cell (DMFC) has been regarded as one of the most promising energy conversion device for portable powers due to their high theoretical energy density, simple system design, and easy fuel storage and transport [1]. However, the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) and the material corrosion issue in the currently adapted strong-acid environment are hindering the DMFC application. Hence, researches have been widely carried out to develop direct methanol alkaline fuel cell (DMAFC) with faster electrode kinetics and less material corrosion [2–4].

Precious metals, especially the platinum group metals are the currently used cathode catalyst for DMAFC [5,6]. Although state-of-the art Pt-based catalyst has superior ORR activity, the limited resource and high cost hamper its large-scale application. On the other hand, due to anode methanol penetration, oxygen reduction and methanol oxidation simultaneously occur on the Pt surface, forming “cathodic mixed potential” and decreasing the cell performance [7–9]. Therefore, the exploration of cost-effective, methanol-tolerant, and efficient alternatives of Pt and Pt-based catalysts are crucial for the development of DMAFC. Owing to the inherently faster electrode kinetics and less corrosive condition in alkaline media, many alternative materials have been investigated as ORR catalysts for DMAFC. Since Jasinski [10] reported the cobalt phthalocyanine could be used as ORR catalyst in 35% KOH in 1964, various materials including chalcogenides [11], transition metal macrocyclic compounds

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* *Corresponding author*. Tel.: +86 411 84379072; fax: +86 411 84665057.
** *Corresponding author*. Tel.: +86 411 84379935.
E-mail addresses: zhanghm@dicp.ac.cn (H. Zhang), zhonghexiang@dicp.ac.cn (H. Zhong).

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[12–14], metallic oxides [15–17], nitrides and carbides [18,19], and doped carbon materials [20] have subsequently been proposed as promising catalysts for the ORR in alkaline media.

Among the non-precious metal catalysts, carbon materials doped with heteroatom have received considerable attention lately due to their high ORR activity, superior stability, excellent electron conductivity, versatile structure, and low cost [21,22]. Nitrogen atom is often chosen as the doped atom for its close atom number and unique valence bond structure compared with carbon atom [23]. The introduction of nitrogen atoms into the carbon material breaks the electroneutrality to create positive charge density on the adjacent C atoms [22,24], changes the chemisorptions mode of oxygen, and consequently enhances the ORR activity. In alkaline media, nitrogen doped carbon material show pronounced catalytic activity, which is close to or even surpassing the Pt-based catalysts. Gong et al. [24] reported that the vertically aligned nitrogen-doped carbon nanotubes-arrays (VA-NCNTs) exhibited better electrocatalytic activity and stability than Pt/C in alkaline media. Recently, nitrogen-doped carbon materials such as nitrogen-doped carbon nanotubes [23,25–27], nitrogen-doped graphene and graphitic arrays [28–31], and nitrogen-contained polymer functionalized carbon [32], nitrogen-doped hollow carbon [33,34], are also reported with outstanding ORR activity and electrochemical stability.

Carbon aerogels and carbon xerogels possess controllable three-dimensional structure and high surface area. They are widely used as hydrogen storage materials, adsorbents, double-layer capacitor materials, and catalyst supports [35–38]. Our previous work demonstrates that the nitrogen-doped carbon xerogel is promising for use as ORR catalyst in acid media [39], which was featured of high activity and superior stability in proton exchange membrane fuel cells. However, to our best knowledge, the application of nitrogen-doped carbon xerogel as ORR catalyst in alkaline media was seldom report. In this work, we adopt the nitrogen-doped carbon xerogel (NCX) as ORR catalyst for DMAFC, investigating its ORR activity and selectivity in methanol contained electrolyte. Results show that NCX presents high ORR activity, stability and excellent methanol tolerance.

2. Experimental

2.1. Catalyst preparation

The NCX catalysts were prepared according to our previous work [39]. Briefly, 6.16 g resorcinol (R) was dissolved in 7 ml deionized water and mixed with 8.4 ml formaldehyde (F) solution (37% formaldehyde, aq.). Co $(NO_3)_2 \cdot 6H_2O$ (C) with designed molar ratio (R/C), followed by continuous stir to form a uniform and pink mixture. The polymerization of RF was initiated by the addition of 4 ml ammonia solution (28% NH_3, aq.) drop by drop. Then the polymer was cured at

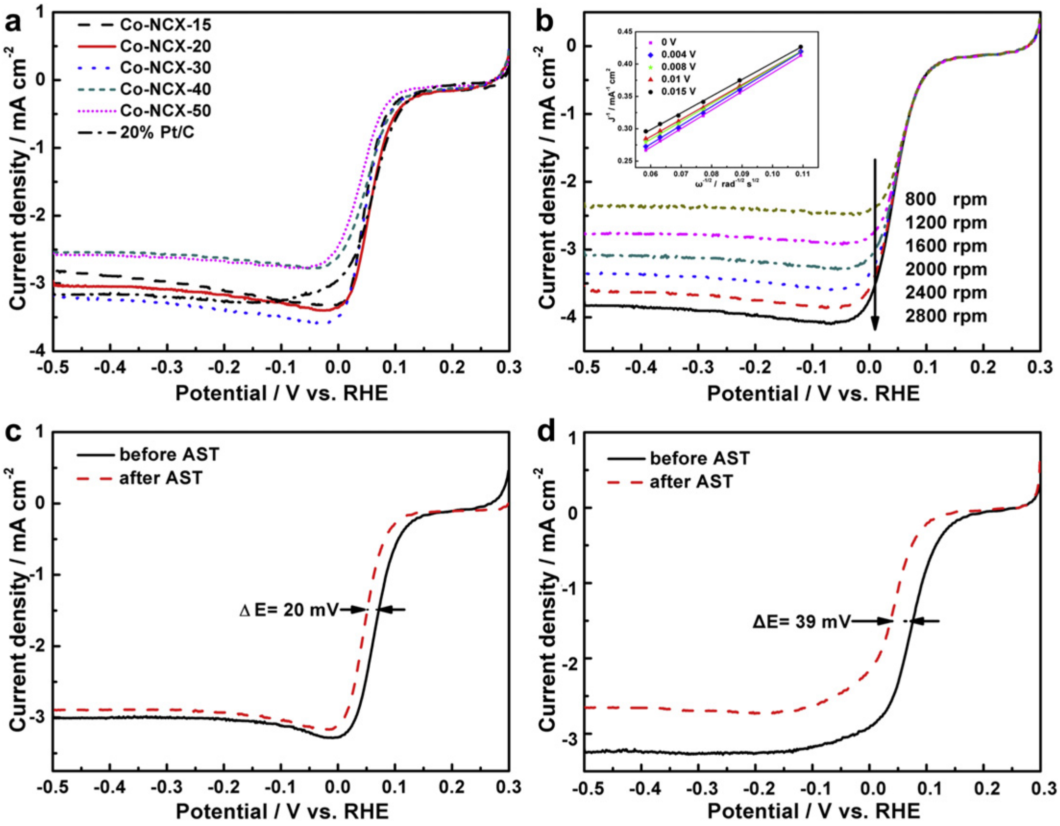

Fig. 1 – Polarization curves for (a) Co-NCX catalysts with different R/C value in comparison with Pt/C; (b) Co-NCX-20 at various rotating rates and Koutecky–Levich plot recorded at selected potentials; (c) Co-NCX-20 and (d) Pt/C before and after AST. Potential range: from −0.5 V to 0.3 V vs. RHE. Scan rate: 5 mV s^{-1}. Electrolyte: O_2 saturated 1 M NaOH. Rotating speed: 1600 rpm (except (b)).