



Active sites and mechanism on nitrogen-doped carbon catalyst for hydrogen evolution reaction



Gui-fa Long^a, Kai Wan^a, Ming-yao Liu^a, Zhen-xing Liang^{a,*}, Jin-hua Piao^b, Panagiotis Tsiakaras^{c,d,*}

^a Key Laboratory on Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, PR China

^b School of Food Science and Engineering, South China University of Technology, Guangzhou 510641, PR China

^c Department of Mechanical Engineering, School of Engineering, University of Thessaly, Pedion Areos, 38334 Volos, Greece

^d Laboratory of Electrochemical Devices based on Solid Oxide Proton Electrolytes, Institute of High Temperature Electrochemistry, Russian Academy of Sciences, Yekaterinburg 620990, Russia

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ABSTRACT

The nature of active sites and mechanism of hydrogen evolution reaction (HER) on the nitrogen-doped carbon catalyst is extensively investigated, by combining physicochemical and electrochemical methods. Two carbon catalysts, with the same chemical nature but different nitrogen content, are employed in this investigation. Electrochemical methods are applied to investigate the electrochemical behavior at different pH values (1.0–2.0, 12.0–13.0). It is found that increasing nitrogen content has a positive effect on the electrocatalytic activity, and therefore, the doped nitrogen atoms should be the active sites. The kinetic current, normalized by the surface nitrogen content, is found to be the same for the two catalysts, confirming the above claim. As such, HER is proposed to proceed on these active sites by the Volmer-Heyrovsky mechanism. The electrochemical tests reveal that the electrocatalytic activity closely relies on the solution pH, which is due to the chemical evolution of the active site in different solutions. In acid media, the electrocatalytic activity increases with the concentration of proton, and the Tafel slope is ca. 120 mV dec⁻¹. It is proposed that the electrochemical desorption of proton on the doped nitrogen atoms is the rate determining step (r.d.s.). In alkaline media, the electrocatalytic activity increases with pH, because the increase in pH dramatically enhances the basicity or the surface charge density, thereby facilitating charge transfer and improving activity. In alkaline media, Tafel analysis shows that Heyrovsky step is the rate determining.

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1. Introduction

Hydrogen, as a clean energy carrier, can address the concern on energy sustainability and environmental emissions [1]. Water electrolysis is one of the most effective approaches to generate hydrogen at room temperature [2]. Among a wide variety of available catalysts, Pt and its alloys show the best electrocatalytic activity with an extremely high exchange current density [3–6]. However, its high cost and source scarcity raise great challenges to the large-scale production of hydrogen [7–9]. In response, extensive efforts have been undertaken to develop non-Pt electrocatalysts, including metal alloys [10], carbides [9,11], phosphides [12,13], borides [11], sulfides [14,15], and nitrides [7,16,17].

* Corresponding authors at: Key Laboratory on Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, PR China (Z.-X. Liang) and Department of Mechanical Engineering, School of Engineering, University of Thessaly, Pedion Areos, 38334 Volos, Greece (P. Tsiakaras).

E-mail addresses: zliang@scut.edu.cn (Z.-X. Liang), tsiak@uth.gr (P. Tsiakaras).

Very recently, metal (Co, Mo, Ni)-encapsulated [18–23] and heteroatom (N, S, P)-doped carbon [24–32] represents one new class of non-Pt catalysts for the hydrogen evolution reaction (HER). Qiao et al. [24] found that the nitrogen-doping can dramatically improve the electrocatalytic activity of carbon, and the co-doping with phosphor can further activate the adjacent carbon atom and enhance the reactivity. Moreover, Qiao et al. [25,26] developed interfacial heterogeneous electrocatalysts by integrating C₃N₄ nanolayers with nitrogen-doped graphene sheets. These catalysts exhibited an unbeatable HER performance with a very positive onset potential and remarkable durability. In addition, the electrocatalytic activity could be further improved by doping with multi-heteroatoms (N, S, P) [27,33,34], and the co-doping effect is generally attributed to the so-called synergistic effect.

It should be pointed out that most of the published work is devoted to the material preparation and characterization. Fundamental problems, such as the intrinsic nature of the active site and HER mechanism, have not been well clarified yet. The density functional theory (DFT) calculation is generally used to study

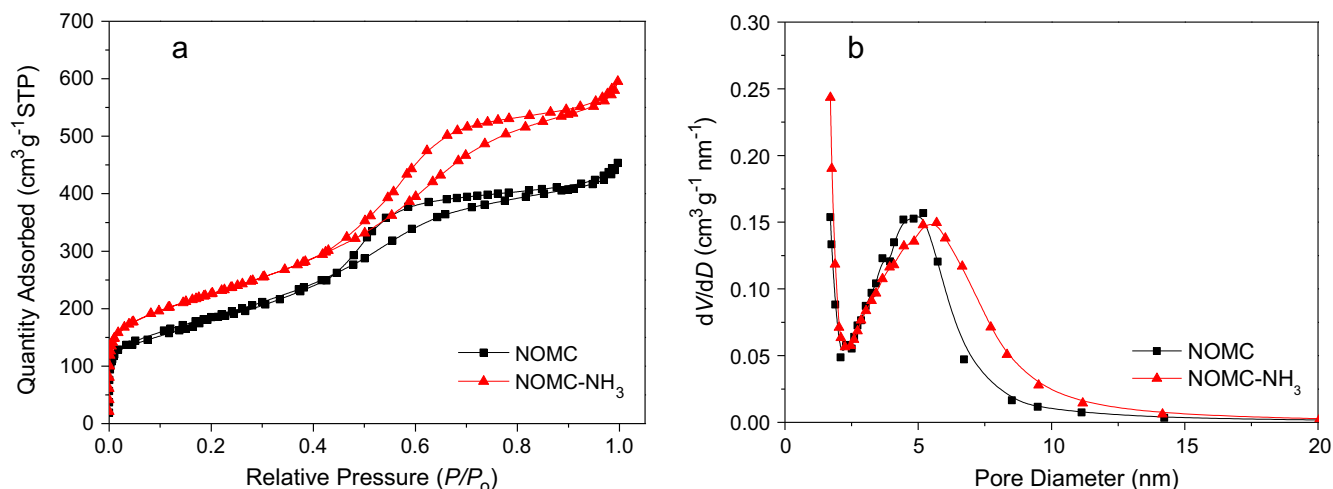


Fig. 1. Nitrogen adsorption/desorption isotherms and pore size distribution of the two nitrogen-doped carbon catalysts: NOMC and NOMC-NH₃.

Table 1

Elemental composition (at.%) of the two carbon catalysts measured by the XPS.

Sample	C 1s	N 1s	O 1s	Fe 2p
NOMC	90.87	4.30	4.65	0.18
NOMC-NH ₃	92.06	6.12	1.63	0.19

the active site and the mechanism [24,25,28,35]; however, it is noted that the results are sometimes inconsistent. The active sites for the hydrogen adsorption are proposed to be either the edge-type nitrogen atoms [25] or the dopant-activated carbon atoms [24].

The phenomenological method is still a realistic way to clarify the active site and mechanism due to the lack of reliable *in-operando* characterization methods. Proton can be used as an electrochemical probe as its concentration is found to yield a paramount effect on the activity. On Pt, the HER proceeds fast in acid media, but it is two orders of magnitude slower in alkaline media [36]. Elbert [37] attributed this finding to the switch of the rate determining step (r.d.s.) from the Tafel step to the Volmer step. In line with this understanding, the core-shell Ru@Pt catalyst, which showed a weaker hydrogen binding energy, behaved much better than did the pure Pt catalyst.

To our knowledge, the pH effect on the nitrogen-doped carbon catalyst for HER has been rarely investigated so far. In our previous work [38], the mechanism of the oxygen reduction reaction was extensively investigated in both acid and alkaline media. In this work, two carbon catalysts, which have basically the same chemical nature except the content of the dopant nitrogen, are used to study the nature of the active sites and the mechanism of the HER. Extensive methods are used to study the evolution in the interfacial structure and the electrochemistry of the catalysts at different pH values. Based on the above results, the nature of active sites and mechanism is proposed in a wide pH window. The findings can both deepen the fundamental understanding on the interfacial electrochemistry of the nitrogen-doped carbon catalyst and guide the development of novel high-performance electrode materials for the HER.

2. Experimental section

2.1. Synthesis of NOMC and NOMC-NH₃

The nitrogen-doped ordered mesoporous carbon (NOMC) material was synthesized by the aid of the nanocasting method. The

details were previously reported [39–43]. Briefly, SBA-15 was initially synthesized in a hydrothermal method using Pluronic P123 as the structure-directing agent. Then, the carbon precursor (pyrrole) was impregnated into SBA-15, which was then polymerized and carbonized at 900 °C in argon. Finally, the SBA-15 template was dissolved out and the NOMC catalyst was obtained.

To increase the nitrogen content, NOMC was subjected to a further calcination at 900 °C for 5 min in ammonia, designated as NOMC-NH₃ in text.

2.2. Electrochemical test

The electrochemical test was performed in a three-electrode cell at 25 °C, using a Zennium and an AMEL 5000 workstation. A gold net and a double junction Hg/HgCl₂ reference electrode were used as the counter and the reference electrodes, respectively. The working electrode was a rotating glassy carbon disk electrode (5.0 mm in diameter). 10 μL of the catalyst ink (10 mg catalyst dispersed in 1.0 mL of 0.84 wt.% Nafion solution) was then dropped onto the disk to make a thin-film electrode, of which the catalyst loading was 0.51 mg cm⁻².

The solutions used in this work were as follows: 0.10 M KOH, 0.050 M KOH, 0.010 M KOH, 0.10 M HClO₄, 0.050 M HClO₄, 0.010 M HClO₄, of which the corresponding pH was 13.01, 12.73, 12.09, 1.12, 1.41 and 2.11, respectively. To decrease the *iR* drop, 0.10 M KNO₃ was added as the supporting electrolyte, and close to the working electrode a Luggin capillary was introduced.

Before the experiments, the solution was vigorously bubbled with argon for 60 min to remove oxygen. Then, cyclic voltammograms (CVs) were carried out at 20 mV s⁻¹ in the potential range of 0 to -0.3 V (vs. reversible hydrogen electrode, RHE). Linear sweeping voltammograms (LSVs) were performed by scanning the potential from -0.3 to 0 V with 5 mV s⁻¹ at 1600 rpm. The HER polarization curve was finally extracted from the LSVs by subtracting the capacitive current.

The accelerated stability tests were performed at room temperature by scanning the potential between 0 and -0.15 V (vs. RHE) at a sweep rate of 100 mV s⁻¹.

The potentiostatic electrochemical impedance spectroscopy (EIS) measurements were performed at an HER overpotential of 0.20 V with the frequency range from 50 kHz to 0.1 Hz.

The electrochemically active surface area was estimated by measuring the non-Faradaic capacitive current at 0.90 V in CV at

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