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To drive Fe-based catalyst towards complete application in proton exchange membrane fuel cells (PEMFCs)

Kai Guo[a], Kun-Ming Shi[a], Jian-Wei Guo[a,*], Xiao-Lin Xie[b,**]

[a] Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China
[b] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

Taking the commercial Pt/C catalyst as a baseline, we disclosed Fe-based catalyst prepared by controlled self-assembly can be used to catalyze hydrogen oxidation reaction (HOR) in the proton exchange membrane fuel cells (PEMFCs). Our electrochemical results clarified that the HOR kinetics is $H_2 \rightarrow 2H_{ad} \rightarrow 2H^+$,which are determined by intermediate H_{ad} species and transfer impacts from H_2 and H^+. Specifically, the Fe-based catalyst can accelerate H_{ad} adsorption/desorption in low potential due to the Fe-H_{ad} reversibility of NPs, and the strengthened mass transfer as well as recoverable active sites of PANI/Fe NPs (polyaniline/Fe NPs) interface in high potential, thus contributing intermittent HOR current in the HOR region. As HOR catalyst, our prototype fuel cell using Fe-based catalyst was demonstrated high E_{OCP}, mass power density and stability in 110 hrs, tolerance for C_3H_8 fuel, promising in replacing Pt-based catalysts in future.

1. INTRODUCTIONS

As promising power for electric-vehicles, the proton exchange membrane fuel cells (PEMFCs) often use Pt-based catalysts in both electrodes reactions as cathode oxygen reduction reaction (ORR) and anode hydrogen oxidation reaction (HOR) [1]. However, Pt resource is scarce and its cost is expensive, it is indispensable to drive PEMFCs by means of non-noble catalysts in future. Currently, some non-noble materials such as Fe and Co species are verified as efficient cathode catalyst, but it is rarely reported as anode catalyst towards hydrogen oxidation reaction (HOR) [1].

Traditionally, the HOR and hydrogen evolution reaction (HER) keep equilibrium near the RHE (reverse hydrogen electrode) potential on Pt metals, and their reversible reaction in acid is simply depicted as: [2]

$$H_2 \leftrightarrow 2H^+ + 2e \qquad (1)$$

This equation is assumed to be composed of two out of three microscopic steps:

$$\text{Tafel step: } H_2 \leftrightarrow 2H_{ad} \qquad (2)$$

$$\text{(3) Heyrovsky step: } H_2 \leftrightarrow H_{ad} + e + H^+$$

$$\text{Volmer step: } H_{ad} \leftrightarrow H^+ + e \qquad (4)$$

Equations (2)–(4) outline the HOR kinetics, and all species including H_2, H_{ad} and H^+ strongly depend on potential and catalyst surface energy, which is difficult to clarify the mechanism in most electrochemical approaches [3–8]. More seriously, the H^+ in solution is traditionally considered to be balanced with the slight soluble H_2 gas, and leads to the intermediate species of H_{ad} adsorption/desorption on material surfaces, indicating a complex diffusion-kinetic process for the multi-species system [9]. Due to the inexplicit HOR kinetic on Pt-based catalysts [10–15], it is a challenge task to explore the non-noble catalyst application in HOR process.

Generally, the H_{ad} is classified as underpotential deposited hydrogen (H_{UPD}) and overpotential deposited hydrogen (H_{OPD}), relating to the HOR and HER regions, respectively. It is important to mention that both H_{UPD} and H_{OPD} can undergo interfacial transfer from the adsorbed state to a subsurface state, and then further transfer from the subsurface state to the absorbed state, reflecting a dynamic material [9]. On highly stable noble materials such as Pt,

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* Corresponding author. Tel.: 86-10-80194009; Fax: 86-10-80194009.
** Corresponding author. Tel: 86-27-87540053(O); Fax: 86-27-87543632.
E-mail addresses: jwguo@mail.tsinghua.edu.cn, jianweiguo@163.com (J.-W. Guo), xlxie@mail.hust.edu.cn (X.-L. Xie).

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Rh, Pd and Ir, as reported the H_{UPD} forms a rigid structure but the H_{OPD} occupies an active structure [16]. Recent studies show that both H_{UPD} and H_{OPD} play active roles, pointing out the H-binding energy as the unique descriptor for the HOR/HER kinetics [2,17]. Because the d-block metals such as Pt, Pd, Ni and Fe have similar potential energy for metal-to-H_{ad}, among them the Fe-group transition metals including Fe, Ni, Co, Cu are considered as potential catalysts though they are unstable under the harsh fuel cell operating condition [9]. Hitherto the HER/HOR behaviors in various media have been reported for shape-controlled transition metal compounds including iron phosphide nanorods (FeP NRs) [18], the ternary metallic CoNiMo [19] and the amorphous alloy CuW [20] catalysts, but the fuel cell validation and mechanism support are lacking. Inspiringly, it has been found that the single-

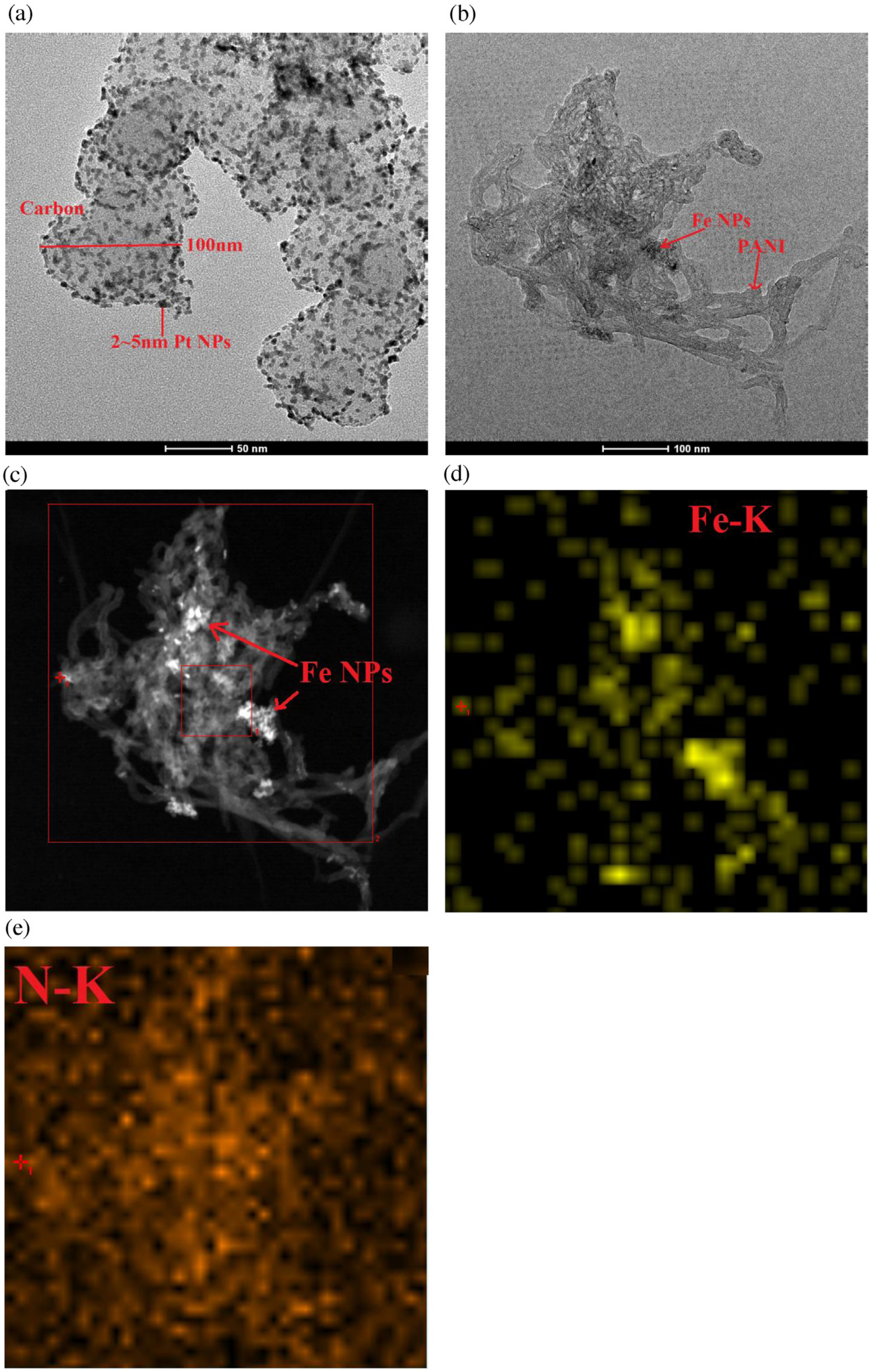

Fig. 1. TEM and STEM: (a) TEM for JM-Pt catalyst; (b,c) TEM and STEM for Fe-based sample; (d ~ e) STEM mapping for Fe-K and N-K distribution, respectively.