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Towards understanding ORR activity and electron-transfer pathway of M-N_x/C electro-catalyst in acidic media

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ABSTRACT

M-N_x/C (M = Fe, Co) type electro-catalyst as a promising alternative to Pt-based electro-catalyst for oxygen reduction reaction (ORR) in fuel cells has been studied for years. However, the mechanism of this four-electron process involving several successive steps and the dynamic intermediate (hydrogen peroxide) participation still remains obscure. In this study, a series of Co-N_x/C with varied densities of Co-N_x sites have been obtained for probing the ORR activity and pathway in acid media *via* adopting zinc ions as a size-comparable template to disperse and regulate Co-N_x sites. Importantly, it has been found that the half-wave potential can be positively correlated with the weight percentage of ionic cobalt species, which suggests the decisive role of the density of Co-N_x sites on ORR activity. More importantly, our results suggest that both Co-N_x/C and 20 wt% Pt/C catalyze ORR *via* two successive steps: ORR begins at the onset potential accompanying the generation of H_2O_2 intermediate, which is more easily to be adsorbed on platinum than on Co-N_x/C surface as detected by ring electrode; Subsequently at the half-wave potential and more negative, H_2O_2 is further reduced immediately and efficiently on platinum, but unfortunately at much lower rate on Co-N_x/C. Thus in addition to improving the initial ORR activity by maximizing the M-N_x coordination, it will be of great significance to endow the non-platinum catalysts with surface active sites capable of adsorbing and efficiently reducing the H_2O_2 intermediate for the complete oxygen reduction to water.

1. Introduction

Oxygen reduction reaction (ORR) is a fundamental process in electro-chemistry and electro-catalysis [1–3]. Unfortunately, the sluggish kinetics of ORR limits the widespread commercialization of fuel cells. It is the high-energy barrier of four-electron transfer process that often leads to considerable amount of byproduct namely hydrogen peroxide and noticeable over-potential [4–6]. Pt-based electro-catalyst is the most active catalyst to date in removing the byproduct and lowering over-potential [7–9], but with extreme high cost. Inspired by biological molecules in nature, M-N_x/C (M = Fe, Co) type electro-catalyst has been found to be as a promising alternative to Pt-based electro-catalyst for several decades [10–12]. Dodelet's group has developed an approach by pyrolyzing the mixture of iron complexes with carbon support in ammonia to synthesize non-PGM electro-catalysts for ORR [13,14]. Jaouen proposed that the active sites of non-PGM electro-catalysts are distributed in the micropores and a high microporosity is essential for high-performance non-PGM electro-catalysts [15,16]. Kramm and Bogdanoff adopted metal oxalate as a template to achieve high porosity and high performance of non-PGM electro-catalysts [17,18].

However, the ORR activity catalyzed by M-N_x/C still falls behind that catalyzed by platinum most probably due to the relatively low density of M-N_x active sites [14]. To enhance ORR activity, it is necessary to fully understand the electro-catalytic role of M-N_x sites in ORR and its correlation with the ORR activity [19,20]. Here we adopt zinc ion [21] as a size-comparable template to disperse and regulate Co-N_x sites, thus a series of Co-N_x/C with varied densities of Co-N_x sites were obtained for probing ORR activity and pathway. It has been found that the as-prepared electro-catalyst with the higher density of Co-N_x sites exhibits higher half-wave potential, and *vice versa*, which suggests that the density of Co-N_x sites plays a decisive role on the half-wave potential.

Furthermore, it is highly significant to trace the production and consumption of hydrogen peroxide dynamically so as to understand ORR in detail considering that hydrogen peroxide as the intermediate of ORR participates in the ORR processes [22–24]. Ioannis Katsounaros used H_2O_2 as a probe to figure out

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"2e pathway" or "4e pathway" catalyzed by platinum as a guide for ORR [25]. Allen J. Bard adopted scanning electrochemistry microscopy (SECM) to quantify the amount of hydrogen peroxide produced on the catalyst surface locally [26]. Atanassov has deciphered the role of several types of active sites (pyrrolic nitrogen, pyridinic nitrogen and Fe-N_x) in ORR pathway [4]. Here by differentiating the value of ring current, we have obtained the production or consumption rate of H_2O_2. It is confirmed that both the as-prepared Co-N_x/C and 20 wt% Pt/C catalyze ORR *via* two successive steps: ORR begins at the onset potential accompanying the production of H_2O_2; Once at the half-wave potential, the consumption, i.e., reduction of H_2O_2 gradually dominates on both Co-N_x/C and platinum, which is premised by the efficient adsorption of H_2O_2 on the surface of the electro-catalysts. The H_2O_2 yield in the medium is the result of competition between the desorption of H_2O_2 from the catalyst's surface into the electrolyte and the reduction of H_2O_2 on the surface, which could be further evaluated in the second step of ORR - hydrogen peroxide reduction, and experimentally confirmed by the current density as the as-obtained current is the sum of the two successive steps. Importantly, M-N_x site is active enough in catalyzing the first reaction at high site density, but relatively kinetically sluggish compared with platinum in reducing the H_2O_2 intermediate regardless of the site density. As the reduction of H_2O_2 plays a decisive role in the second step of ORR at more negative than half-wave potential and is closely related with the surface active sites of the electro-catalyst, it will be of great significance to tune the catalysts with surface active sites in favor of efficiently adsorbing and reducing H_2O_2.

2. Experimental section

2.1. Materials and synthesis

Synthesis of Co-HMs: the synthesis process is the same as described in Ref. [27]. Firstly, HMTA (hexamethylenetetramine) and cobalt nitrate hexahydrate was mixed with the molar ratio of 3:1 in excess water. In addition, the solution was dried at 150 °C for 3 days after stirring for 1 h and the dry sample was grinded into powders and placed on the quartz boat in a tube furnace under N_2 atmosphere. The powders were calcined at different temperatures for 2 h at a heating rate of 5 °C/min from 20 °C to the set temperature (700, 800 or 900 °C). The as-obtained samples were treated in 3 M hydrochloric acid at 80 °C for 10 h to remove the unstable and inactive species and then washed with de-ionized water thoroughly. Finally, the samples were lyophilized and denoted as Co-HM-T-AL (here T represents the set temperature and AL represents after leaching).

Synthesis of CZs: CZs are synthesized *via* template-assisted method compared with Co-HMs. The synthesis process is the same as described above except the amount of precursors. Here large amount of zinc ion is used to serve as the template to disperse cobalt species. To *x*CZ, HMTA, zinc nitrate hexahydrate and cobalt nitrate hexahydrate was mixed with the molar ratio of 3: $(1 - x/100)$: $(x/100)$. For example, to 5CZ, HMTA, zinc nitrate hexahydrate and cobalt nitrate hexahydrate was mixed with the molar ratio of 3:0.95:0.05. The following synthesis procedure is also the same with that of Co-HMs. The pyrolysis temperature of CZs is 800 °C. We controlled the ratio of Co/Zn and finally obtained a series of 5CZ, 10CZ, 15CZ and 20CZ.

2.2. Characterization

The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2250 V diffractometer with a scanning rate of $2^\circ\ \mathrm{min}^{-1}$. The X-ray tube using Cu Kα (λ = 0.154056 nm) radiation was operated at 40 kV and 40 mA. Elemental analysis (C, H, N) was taken on a vario EL cube micro-analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific Escalab 250 spectrometer with Al Kα radiation as the excitation source. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. Transmission electron microscopic (TEM) images was obtained on a JEM-2100F field emission transmission electron microscope operated at 200 kV. Secondary electron images were acquired on a Hitachi S-4800. Agilent 700 Series inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine element concentration. Nitrogen sorption isotherms at 77 K were measured on a Micromeritics ASAP 2020 system. All samples were degassed at 150 °C for 8 h before measurements. The micropore (<2 nm) area and volume were obtain by the t-plot method. The total pore volume was determined from the amount of the nitrogen adsorbed at a relative pressure of 0.99 and the surface area of every sample was calculated by the Brunauer-Emmett-Teller (BET) method from the adsorption data obtained in the relative pressure range of 0.01–1.

2.3. Electrochemical measurements

Cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) analysis were performed on a CHI 760E electrochemical workstation (CH Instrument, Inc.) with a three-electrode cell at room temperature. A platinum wire and an Ag/AgCl (3 M) electrode were used as the counter electrode and the reference electrode, respectively. 0.1 M $HClO_4$ was used as electrolyte for the acidic electrochemical measurement. The catalyst ink was prepared as follows: catalyst (10 mg) and 50 μL of 5 wt% Nafion solution were dispersed in 1 mL isopropanol by sonication to form a homogeneous ink. Then 0.1 M $HClO_4$ electrolyte was purged with O_2 for more than 15 min to provide an O_2 saturated environment before carrying out measurements.

For CV tests, 20 μL of the catalyst ink was cast onto a glassy carbon with an area of $0.2475\ \mathrm{cm}^2$. CV studies were conducted with a scan rate of $50\ \mathrm{mV\ s}^{-1}$.

For RDE tests, 20 μL of the catalyst ink was loaded onto a glassy carbon with an area of $0.2475\ \mathrm{cm}^2$ ($0.81\ \mathrm{mg\ cm}^{-2}$). RDE tests were performed on Pine rotating ring disk electrode apparatus. The steady-state polarization curves were obtained *via* linear scanning voltammetry (LSV) studies, which were first carried out in nitrogen-saturated 0.1 M $HClO_4$ at a rotation speed of 1600 rpm with a scan rate of $5\ \mathrm{mV\ s}^{-1}$ and then carried out in oxygen-saturated 0.1 M $HClO_4$ at a rotation speed of 1600 rpm with a scan rate of $5\ \mathrm{mV\ s}^{-1}$. The steady-state polarization curves were obtained by subtracting data collected in nitrogen-saturated environment from data collected in oxygen-saturated environment.

For RRDE tests, 20 μL of the catalyst ink was cast onto a glassy carbon with an area of $0.2475\ \mathrm{cm}^2$ ($0.81\ \mathrm{mg\ cm}^{-2}$). The steady-state polarization curves were obtained as RDE method. The ring potential was set at 1.05 V versus Ag/AgCl in 0.1 M $HClO_4$. Electron-transfer number and H_2O_2 yield were calculated as the following equations:

$$n = \frac{4I_d}{I_d + I_r/N}$$

$$H_2O_2\% = \frac{200 I_r/N}{I_d + I_r/N}$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring. N was determined to be 0.37 from the reduction of $K_3Fe(CN)_6$.

Commercial 20 wt% Pt/C (platinum supported on Vulcan carbon black, bought from JM, $0.405\ \mathrm{mg\ cm}^{-2}$) was measured for