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Influence of pre-treatment on the catalytic activity of carbon and its Co-based catalyst for oxygen reduction reaction

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ABSTRACT

Impact of carbon pre-treatment on the catalytic activity and selectivity of its own and its relevant non-precious metal Co-based catalyst (carbon-supported cobalt diethylenetriamine, CoDETA/C) for oxygen reduction reaction is investigated. Three pre-treatment methods involving thermal treatment, H₂O₂-oxidation and KOH-activation are used in this paper. Electrochemical activity demonstrated by cyclic voltammograms and rotating ring disk electrode technique in O₂-saturated electrolyte shows that pre-treatment step has a significant effect on the catalytic activity and selectivity of carbon and its Co-based catalyst: (1) for carbon sample, a KOH-activation gives the highest activity in acid medium, while a H₂O₂-oxidation in alkaline solution; and (2) for its Co-based catalyst, the as-ground gives the highest activity and selectivity in acid solution, while a KOH-activation in alkaline medium. Raman spectra indicate that pre-treatment can decrease the disorder of carbon matrix. X-ray diffraction shows that face-centered cubic α -Co phases are present and pre-treatment of carbon can decrease the size of metal Co dispersed on the catalyst surface.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been recognized as the most promising energy converting devices in terms of zero emissions and high efficiency by converting stored hydrogen into electricity. In practice, they need Pt and Pt-alloy catalysts to promote hydrogen oxidation reaction at the anode and oxygen reduction reaction (ORR) at the cathode. Due to the slow kinetics of the ORR, there must be higher loading of Pt at the cathode than at the anode to promote their performance. However, the expensive cost, limited supply

and poor durability of Pt are the major barriers to mass-market fuel cells for commercial applications. Thus, numerous efforts have been made to develop non-precious metal catalysts to replace Pt and Pt-based catalysts for the ORR [1–5]. Among them, heat-treated carbon supported non-precious metal (especially Co and Fe) complexes with macrocyclic ligands, such as porphyrins and phthalocyanines that contain four nitrogen donors (MN₄ chelates), have been expected to be the most promising catalysts [6–8], since Jahnke showed the beneficial effects of heat-treatment in an inert atmosphere to improve their catalytic activity and chemical stability [9]. Heat-treated metallophthalocyanines

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are also active catalysts for the ORR in alkaline membrane fuel cells, such as carbon nanotube supported Co and Fe phthalocyanine [10]. Moreover, Kannan and co-workers reported that the CoPc/MWCNT catalyst showed a higher catalytic activity than the FePc/MWCNT catalyst in alkaline solution [10].

However, it has been demonstrated that the expensive macrocycle ligands were not necessary to obtain these ORR catalysts by pyrolysis conditions. Following this approach, many non-precious metal catalysts have been synthesized using various inexpensive nitrogen-containing compounds [11–15]. For example, heat-treated mixtures of nitrogen-containing precursor, such as ethylenediamine [11,12], phenantroline [13], cyanamide [14] and di-quinolyldiamine [15], together with Fe or Co salt were considered as the promising ORR catalysts.

Despite there are numerous studies in the world, the active sites of these ORR catalysts are not clear and heavily debated in the literature [16–20]. For example, employing NH_3 and CH_3CN as nitrogen precursors, based on the time-of-flight secondary ion mass spectrometry results, Dodelet and co-workers claimed that origins of the high catalytic activity, especially the catalytic active sites responsible for this performance after heat treatment were the CoN_4/C moiety [16]. Popov's group proposed that active sites with pyridinic nitrogen were responsible for the catalytic ORR activity [17], whereas they also reported that quinone groups introduced by nitric acid treatment, in addition to increasing the dispersion of the Co-based chelate complexes, played a role in forming the active site for oxygen reduction [18]. Atanassov and co-workers proposed a dual-functionality active site where O_2 was initially reduced at a Co^{2+} containing N–C type site in a 2e process to form HO_2^- , which could react further in the series type ORR mechanism at the decorating $\text{Co}_x\text{O}_y/\text{C}$ surface nanoparticle phase [19]. Oh and co-worker examined the role of transition metals (Co and Fe) on nitrogen-modified carbon-based catalysts synthesized by the pyrolysis process in the presence of polypyrrole (PPy) and ethylenediamine (EDA) with different amounts of transition metals [20]. The results indicated that transition metal itself did not behave as an active site for ORR, while the total nitrogen content and the active nitrogen functional groups, such as pyridinic-N and graphitic-N, were strongly dependent on the type of transition metal and the amount of transition metal used [20]. They also believed that transition metal served to catalyze the formation of active nitrogen functional groups for the ORR by doping nitrogen into carbon [20].

Although the exact nature of the active sites for the ORR of these ORR catalysts is not yet clear, it is believed that there are several elements influencing the catalytic activity of these non-precious metal catalysts: (1) nature of the metal and its precursor as well as nature of the nitrogen precursor, (2) carbon support and (3) heat-treatment strategy. As far as the second point is concerned, pre-treatment of carbon support can affect its fundamental property, such as acid-base property, loading level of catalyst, number of catalytic sites, distribution of catalyst particles, and so on. For example, thermal treatment of carbon was usually conducted in the presence of gases and in the presence or absence of organic or inorganic additives to cause a “burn-off” and thereby altered the physicochemical properties [21–23]. Some studies have also pre-treated carbon with HNO_3 before the heat-treatment in

the presence of an N-containing precursor [18,24]. Higher ORR catalytic activity was observed after this step was taken. It was explained that the oxidized carbon surface had more oxygen-based functionalities, such as quinone groups, which favored the adsorption of amines and increased the polarity of the carbon support, and this led to a better dispersion of metal ion on the surface, resulting in higher catalytic activity [18]. Dodelet and co-workers have studied the main structural parameters which influenced the catalytic active site on the carbon support and found that the larger the amount of disordered phase in the pristine carbon the better the catalytic activity for the ORR of the resulting catalyst, for that NH_3 reacted mainly with the disorganized carbon, leaving nitrogen at the surface of the support [25–28]. He reported that KOH activation was an effective way to decorate MWCNTs' surface with oxygen-containing groups and bigger surface area, which made them more suitable as catalyst support materials [29].

Our group has studied non-precious metal ORR catalyst for a long time. During the past five years, we have systematically studied a novel class of MTETA/C catalysts ($M = \text{Fe}$ and Co) based on the small ring MN_4 structure prepared from pyrolyzing carbon-supported metal triethylenetetramine chelate in Ar atmosphere, including the effect of pyrolyzing temperature, metal loadings and metal precursors on the catalytic activity for the ORR [30–36]. Recently, we have reported a family of promising non-precious metal oxygen reduction catalyst (CoDETA/C) by using a N_3 structure diethylenetriamine ligand [37]. For this CoDETA/C catalyst, our group has already investigated the effect of pyrolysis temperature and atmosphere on its ORR performance and selectivity [37,38]. We have also studied the influence of rotating rates (from 100 to 1600 rpm) on its ORR performance and selectivity [37].

As we all know, hydrogen peroxide (H_2O_2) is an environmental oxidant with its product of water. It is also a by-product in the ORR process and can corrode the catalyst even inactivate it. On the other hand, KOH-activation is also an effective route to improve the specific surface area and pore size distribution of carbon, facilitating the access of the active phase during catalyst preparation. Furthermore, KOH (corrosion) solution is an electrolyte in alkaline membrane fuel cell. If we treat carbon support by H_2O_2 or KOH solution in advance and this can avoid the corrosion situation. As far as we known, many studies have been done to optimize the pre-treatment step for Pt-based catalysts, few research has been carried out to study and compare the effect of H_2O_2 -oxidation and KOH-activation on the catalytic activity of non-precious metal catalyst. With this in mind, here, we use three different pre-treatment methods involving thermal treatment, H_2O_2 -oxidation and KOH-activation to explore the effects of carbon pre-treatment on the catalytic activity and structure of its own and its relevant non-precious metal Co-based catalyst. The non-precious metal Co-based catalyst is synthesized pyrolyzing carbon-supported cobalt diethylenetriamine chelate at 800 °C in Ar atmosphere [37,38]. The catalysts are characterized by X-ray diffraction (XRD) and Raman spectra. Catalytic activities for the ORR are demonstrated by cyclic voltammograms (CVs) and rotating ring disk electrode (RRDE) measurements in O_2 -saturated acid and alkaline solution at room temperature.

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