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N,N'-Bis(salicylidene)ethylenediamine as a nitrogen-rich precursor to synthesize electrocatalysts with high methanol-tolerance for polymer electrolyte membrane fuel cell oxygen reduction reaction

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HIGHLIGHTS

- Co–N–S/C catalysts for ORR are synthesized using salen as N-ligand by pyrolyzing process.
- The overall electron transfer numbers for the catalyzed ORR are 3.6–3.9 with 3.7–19.9% %H_2O_2 yield.
- The graphitic-N groups are found to be the most active sites for ORR activity.
- These Co–N–S/C catalysts exhibit the superior methanol tolerance to commercial 40% Pt/C.

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ABSTRACT

A cost-effective chemical, N,N'-bis(salicylidene)ethylenediamine (salen), is used as a ligand to form a carbon-supported Co-salen complex (Co-salen/C) by a simple solid-sate reaction. The Co-salen/C is then pyrolyzed at 600, 700, 800, 900, and 1000 °C to form carbon-supported Co–N–S/C catalysts for the oxygen reduction reaction (ORR). XRD, EDX, TEM, and XPS are used to characterize the catalysts' composition, crystalline nature, morphology, and possible surface groups induced by heat-treatment. Investigation of the catalytic activity and the ORR mechanisms using rotating disk electrode and rotating ring-disk electrode techniques demonstrates that all of these Co–N–S/C catalysts are highly active for the ORR in an O_2-saturated 0.1 M KOH solution, but the catalyst heat treated at 700 °C gives the best ORR activity. The overall electron transfer number for the catalyzed ORR was determined to be 3.6–3.9, with 3.7–19.9% H_2O_2 production over the potential range of −0.05 to −0.60 V, suggesting that the ORR catalyzed by Co–N–S/C catalysts is dominated by a 4-electron transfer pathway from O_2 to H_2O. In addition, these catalysts exhibit superior methanol tolerance to commercial 40% Pt/C catalyst, thus the Co–N–S/C catalysts are promising for use as electrocatalysts in alkaline polymer electrolyte membrane fuel cells.

1. Introduction

In both acidic and alkaline polymer electrolyte membrane (PEM) fuel cells and in metal-air batteries, the catalytic cathode oxygen reduction reaction (ORR) is more challenging than the anode fuel or metal oxidation reactions, because it dominates the devices' performance in terms of both power density and durability [1,2]. In the current state of technology, Pt-based catalysts must be used to catalyze the slow ORR to make PEM fuel cells technically feasible

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and practical. However, due to the need for high Pt loadings at fuel cell cathodes, and Pt catalysts' low fuel tolerance (e.g., in direct alcohol fuel cells) [3,4], it is advisable to replace Pt with non-precious metal catalysts [5].

In recent years, alkaline PEM fuel cells have been recognized as feasible energy conversion devices for several reasons [6–8]. One of their major advantages is the possible usage of non-noble metal catalysts for the ORR. These catalysts are cost-effective and at the same time fuel tolerant. In a direct alcohol fuel cell, for example, due to unavoidable fuel crossover from anode to cathode, it is highly desirable that the cathode catalyst not have catalytic activity towards the fuel. If the cathode catalyst is catalytically active toward fuel oxidation (meaning it has no fuel tolerance), either the cathodic O_2 reduction potential of the corresponding fuel cell will be depressed or the fuel efficiency will be reduced. Using alkaline PEM fuel cells, this issue of fuel crossover can be lessened. This is because the conduction ion in an alkaline PEM fuel cell membrane (the anion exchange membrane) is OH^-, which transfers from cathode to anode during operation – in the opposite direction of fuel crossover, which proceeds from anode to cathode – leading to much less fuel crossover than in acidic PEM fuel cells, where the direction of proton transfer is the same as that of fuel crossover [6]. Therefore, using an alkaline PEM fuel cell catalyzed by a fuel-tolerant cathode catalyst will be highly beneficial to fuel cell performance and fuel efficiency.

In fact, since Jasinski first observed that cobalt phthalocyanine could catalyze the ORR in an alkaline medium [9], intensive research has been conducted to explore transition metal macrocycles as cathode catalysts for the ORR. However, poor stability is their major disadvantage. It was reported that the stability can be greatly improved by using heat-treatment procedures. The enhancement can be attributed to lower production of hydrogen peroxide, which is capable of oxidizing and splitting the active sites. Although significant progress has been achieved with heat-treated macrocyclic compounds as ORR catalysts, the activity and stability of such catalysts are still insufficient to replace Pt at the fuel cell cathode. Moreover, transition metal macrocycles are still expensive because their synthesis is complex. A significant breakthrough was made by Yeager et al. [10], who demonstrated that expensive macrocycles could be substituted by individual metal and N precursors. Since then, many simple and cost-effective nitrogen-containing ligands for metal-complex catalysts have been explored, such as polypyrrole [11,12], ethylene diamine [13], cyanamide [14], and phenanthroline [15]. Although the nature of the active ORR catalytic sites in such M–N–C catalysts is still not entirely understood, it is widely accepted that the ORR performance of these catalysts strongly depends on the type of nitrogen and transition-metal precursors used, the heat-treatment temperature, the carbon support, and the synthesis conditions [16,17]. Therefore, further exploring new materials and optimizing catalyst synthesis conditions to achieve highly active and stable non-precious metal catalysts is definitely necessary [18].

Most recently, using pyridine as a nitrogen-rich ligand and cobalt sulfate heptahydrate as a metal precursor, we synthesized carbon-supported Co-nitrogen catalysts (CoPy/C) that are highly active for the ORR after high-temperature treatment [19]. These synthetic catalysts thus offer tremendous potential for achieving better functionality than Pt by manipulating the catalysts' active components. In a continuation of this effort, we here demonstrate that *N*,*N*′-bis(salicylidene)-ethylenediamine (salen), as a new promoter, can significantly enhance the electrocatalytic activity of the Co site, due to the formation of carbon-supported Co–N–S catalysts after heat-treatment. Unlike pyridine, salen contains two nitrogen atoms that can form a chelate structure with metal Co, thereby making the active sites more available, even though the relative nitrogen content of Co-salen is lower than that of Co-pyridine. We used several instrumentation methods–powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, as well as X-ray photoelectron spectroscopy (XPS) – to characterize the structure and composition of the catalysts and thereby obtain insight into their ORR catalytic activity and its dependence on heat-treatment temperature. The reaction kinetics and mechanism of the ORR on these materials were analyzed in oxygen-saturated alkaline solutions by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques as well as rotating ring-disk electrode (RRDE) measurements. The ORR catalyzed by Co–N–S/C catalysts in the presence of methanol was also studied and compared with commercially available Pt/C to evaluate the applicability of Co–N–S/C in direct methanol alkaline fuel cells.

2. Experimental

2.1. Materials and catalyst synthesis

For catalyst synthesis, the following starting materials were used: *N*,*N*′-bis(salicylidene)ethylenediamine (salen) (analytic grade, Aldrich), cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$) (analytic grade, Aldrich), methanol (analytic grade, Aldrich), and Vulcan XC72R carbon black (Cabot Corporation, $S_{BET} = 236.8\ m^2\ g^{-1}$). All of these materials were used without further purification. The catalysts in this study were synthesized using a solid-state reaction. In a typical synthesis, a mixture of 0.143 g $CoSO_4$ $7H_2O$, 0.075 g salen, and 0.180 g XC72R carbon black were mixed with 20 ml methanol, carefully milled for about 2 h in a mortar, and then vacuum dried at 40 °C for 1 h. In this process, a chemical reaction between Co(II) ion and salen ligand occurred on the carbon particles, forming carbon-supported Co(II)-salen complex (abbreviated as Co-salen/C). This powder was then placed in a crystal boat and heat treated at 600, 700, 800, 900, and 1000 °C, in each instance for 2 h under N_2 atmosphere. Analysis using XRD, EDX, and XPS showed that the catalysts formed after heat-treatment contained Co, C, N, S, and O, thus we denote these catalysts as Co–N–S/C-*T*, where *T* is the heat-treatment temperature.

2.2. Instrument characterizations

The crystallinity of the various catalyst samples was determined by XRD using a Rigaku D/max-2550 V diffractometer with Cu Kα radiation operating at 30 kV and 40 mA. TEM analyses were performed on a high-resolution Hitachi JEM-2100 system operating at 200 kV. The catalyst bulk composition was verified by means of EDX. Surface analysis of the catalyst particles was carried out by XPS on an RBD-upgraded PHI-5000C ECSA system (PerkinElmer) with an Al K X-ray anode source ($h\nu = 1486.6$ eV) at 14.0 kV and 250 W.

2.3. Electrochemical measurements

The catalysts' performance for the ORR was measured in a thermostat-controlled, standard three-electrode cell at room temperature with a Pt-wire counter electrode, a saturated calomel electrode (SCE) reference electrode, and a rotating glassy carbon (GC) disk electrode as the working electrode. For catalyst-layer preparation on the working electrode surface, please refer to our recent publication [19]. Prior to the ORR experiments, the electrolyte was deaerated by bubbling with N_2 for at least 30 min. Steady cyclic voltammograms were obtained at a scan rate of 50 mV s^{-1} within an electrode potential range of −0.3 to 0.8 V vs. standard hydrogen electrode (SHE). For the ORR measurements using a RDE,