



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Electrochemical catalytic contribution of transition metals at the center of porphyrin macrocycle structures as catalysts for oxygen reduction reaction

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ARTICLE INFO

Article history:

Received 13 May 2017
Received in revised form 30 May 2017
Accepted 30 May 2017
Available online xxx

Keywords:

Porphyrin macrocycle structure
Non-precious catalyst
Electrochemical polymerization
Oxygen reduction reaction

ABSTRACT

In a macrocyclic structure, the contribution of the metal- N_4 sites to oxygen reduction reaction (ORR) remains controversial. In this study, to investigate the contribution of macrocyclic cathode catalysts to the ORR properties in the macrocyclic sites excluding various synthetic conditions, the macrocyclic cathode catalysts were prepared using an electrochemical polymerization method at room temperature. The ORR activity of the deposited electrodes as catalysts was evaluated in an alkaline medium. To clarify the core metal as an active site in the macrocyclic structure as a cathode catalyst for the ORR, a CN^- -poisoning test of core metal site was performed.

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Introduction

Fuel cells are a renewable energy system, which can efficiently convert hydrogen as a chemical fuel into electricity [1–3]. In general, hydrogen and oxygen can be electrochemically oxidized and reduced at an anode and a cathode, respectively, producing water as a by-product. Oxygen reduction reaction (ORR) at a cathode is known to be extremely sluggish, compared to hydrogen oxidation reaction at an anode; the rate-determining-step is thus needed in the fuel cells [4–6]. Currently, although platinum (Pt) has disadvantages such as fairly high overpotential loss, CO-poisoning effect, and limitation of reserves, Pt has been utilized as an excellent cathode catalyst for the ORR [1,4]. Thus, non-precious metal (NPM) cathode catalysts as an alternative to Pt have been intensively studied [7–11]. In 1964, cobalt phthalocyanine (Pc) as a NPM catalyst was considered to exhibit an ORR activity due to the macrocyclic metal- N_4 in the Pc which could play a role as a catalytic active site [12]. In particular, among the macrocycle structures, the macrocyclic catalysts containing various core metals such as Co and Fe have shown considerably improved ORR performance, compared to core metal-free macrocycles. The catalytic sites in the macrocyclic cathode catalysts for ORR are still controversial [4,13–21]. However, it was reported that the catalytic

activity of the macrocycle structures might be significantly dependent on various synthetic conditions such as reaction temperature and atmosphere.

In this study, to investigate the contribution of macrocyclic cathode catalysts to the ORR activity in the macrocyclic metal- N_4 sites excluding various synthetic conditions, the macrocyclic cathode catalysts were readily prepared using an electrochemical polymerization method at room temperature; i.e. an electrochemical technique that can be used for synthesis of solid-state polymer by applying an oxidative potential to the end group of the monomer in solution [22–33]. Thus, the metal- N_4 sites in the macrocyclic catalysts prepared using an electrochemical polymerization method at a relatively mild synthetic condition could be relatively less affected and well conserved compared to macrocyclic catalysts synthesized at a harsh atmosphere such as high temperature of $>900^\circ\text{C}$. Electrodes having the Co- N_4 and Fe- N_4 sites were fabricated using an electrochemical polymerization method with CoTMPP (5,10,15,20-Tetrakis(4-methoxyphenyl)porphinate cobalt(II)) and FeTMPP (5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphine iron(III) chloride), respectively. For comparison, an electrode having the N_4 sites in the absence of core metals was prepared using an electrochemical polymerization method with TMPP (5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphine). The electrochemical properties and ORR activity of the as-prepared electrodes were evaluated and compared in an alkaline medium.

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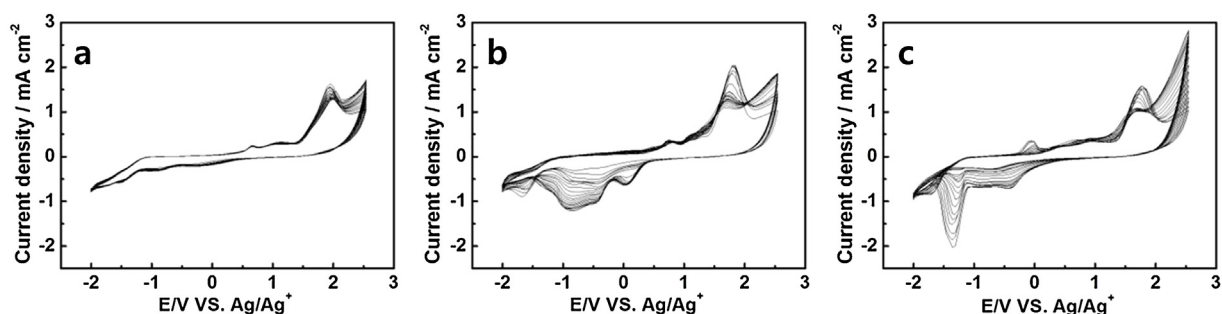


Fig. 1. CVs of the samples deposited on the GC electrodes during electropolymerization process with (a) TMPP, (b) FeTMPP, and (c) CoTMPP in dichloromethane media in the potential range of $-2.0 \sim 2.5$ V with a scan rate of 50 mV s^{-1} for 100 cycles.

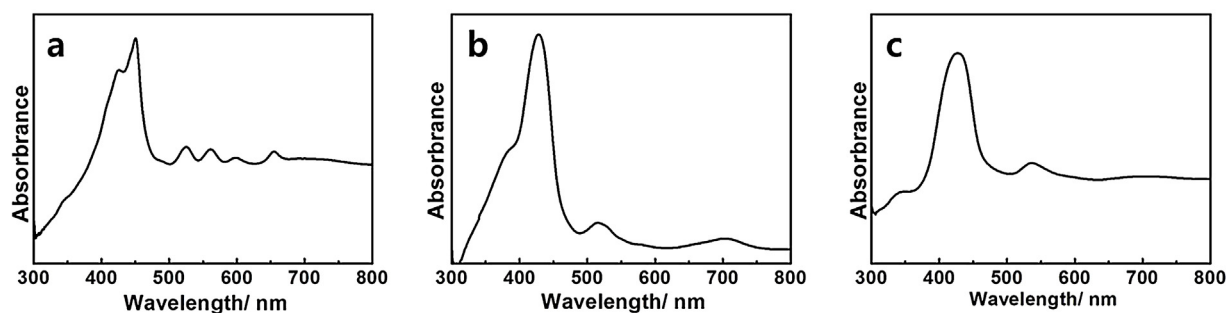


Fig. 2. UV-vis absorbance spectra of (a) EP-TMPP, (b) EP-FeTMPP, and (c) EP-CoTMPP.

Experimental

Preparation of the electrodes

1 mM precursor solutions for electrochemical polymerization were prepared by dissolving TMPP (Sigma Aldrich, 95%), CoTMPP (TCI, >96%), and FeTMPP (Sigma Aldrich, 98%) with 0.1 M tetrabutylammonium tetrafluoroborate (Sigma Aldrich). Glassy carbon (GC) and fluorine doped tin oxide (FTO) glass were used as the working electrodes for electrochemical characterization and UV-vis analysis. The as-prepared electrodes were rinsed with CH_2Cl_2 solution in order to remove any non-reacted materials on the electrodes and were then dried in a 50°C oven for 10 min.

Materials characterization

To qualitatively investigate the chemical structure of the as-deposited samples on the FTO glass, UV-vis absorbance analysis was performed using UV-vis absorbance spectroscopy (JASCO, V-650) in the range of 300–800 nm at a scan rate of 200 nm min^{-1} . The morphology of the samples was observed using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-7800F) at 5 kV. The electrochemical properties of the electrodes were measured using a potentiostat (CH Instrument, CHI 700C) in a three-electrode electrochemical cell. The deposited GC, Ag/AgCl (saturated in 3M KCl), and graphitic rod were used as working, reference and counter electrodes, respectively. Cyclic

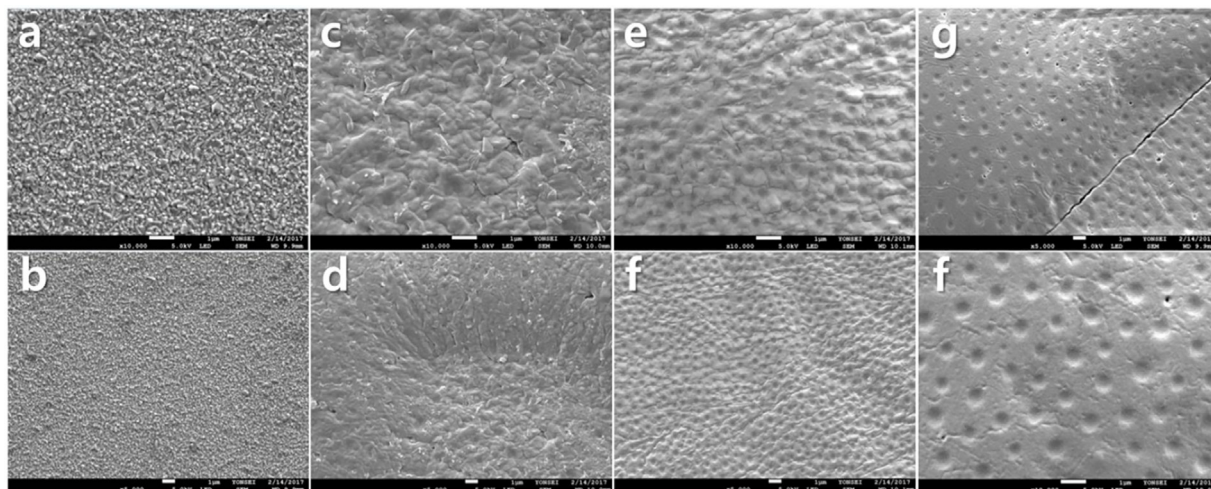


Fig. 3. SEM images of FTO glass (a),(b), EP-TMPP (c),(d), EP-FeTMPP (e),(f), and EP-CoTMPP (g),(h).

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