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Lithium manganese phosphate-carbon composite as a highly active and durable electrocatalyst for oxygen reduction reaction



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ABSTRACT

Development of Pt-free electrocatalysts for oxygen reduction reaction (ORR) is one of the most important tasks for fuel cell commercialization. Various Mn compounds have been proposed as catalysts for ORR, but poor activity and stability necessitate further advances for their practical utilization. In this study, we demonstrate a lithium manganese phosphate-carbon composite (LMP-C) as a highly active and durable electrocatalyst for ORR in alkaline medium. LMP-C, synthesized by the solid-state method, exhibited significantly enhanced electrical conductivity and electrochemical properties, which led to a substantial increase in ORR performance. Comparison between LMP-C and the manganese phosphate-carbon composite, based on various physicochemical characterizations, revealed a high preference for the formation of the Mn³⁺ state on the surface of LMP-C that resulted in effective charge transfer during oxygen reduction. Moreover, the excellent stability of LMP-C was confirmed by carrying out 3000 cycles of the accelerated durability test, in which no drop in ORR performance was observed.

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1. Introduction

Fuel cells, based on the electrochemical reaction of hydrogen and oxygen to generate water, are one of the most promising energy conversion devices for sustainable production of electrical energy. In the operation of fuel cells, the oxygen reduction reaction (ORR) rate limits the overall performance due to its four electron based sluggish kinetics. Therefore, in order to facilitate practical and commercial applications of fuel cells, various efforts have been made to develop electrocatalysts with superior activity for ORR [1– 4]. In the past decades, substantial improvements in activity and

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http://dx.doi.org/10.1016/j.electacta.2017.05.131 0013-4686/© 2017 Elsevier Ltd. All rights reserved. durability have been achieved by tailoring the physicochemical properties of state-of-the-art Pt catalysts [5–11]. Until recently, research on fuel cell catalysts was mainly focused on ORR in acidic medium because of the limited choices in ion conducting membranes (e.g., Nafion for proton conduction). However, rapid advances in development of membranes for hydroxyl ion conduction resulted in investigation of ORR in alkaline electrolytes [12–15]. Due to the difference in adsorption strengths of spectators and intermediate species on active sites of catalyst, oxygen reduction shows decreased kinetic barrier in alkaline media [16,17]. Consequently, there is a wider variety of possible ORR catalysts in alkaline medium compared to in acidic medium, including carbonaceous materials and non-noble metal compounds [18,19].

Among numerous low-cost ORR catalysts being investigated in order to replace Pt, Mn compounds have received attention due to their feasibility for various chemical modifications [20–36]. Following the pioneering work by Lima et al. in 2006, wherein MnO_x nanoparticles deposited on a carbon support were directly utilized as electrocatalysts [20], Mn oxides with controlled morphology and crystallinity have been reported [21–23].

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Furthermore, Mn compounds prepared by alloying or hybridization with other metals have been verified to be effective for ORR application, and the synergistic effect by N-doped carbon supports has also been studied [24–35].

In this study, we demonstrate, to the best of our knowledge, for the first time the feasibility of using LiMnPO₄ as an ORR catalyst in an alkaline medium. As discussed above. Mn compound catalysts were applied in ORR due to its favorable characteristics, but they often suffer from insufficient long-term stability [24,36]. Among Mn-based materials, LiMnPO₄, which is an olivine-type phosphate material, has superior stability compared to bare oxides due to the P-O bonds that provide structural durability [37,38]. However, due to its low electronic and ionic conductivity, LiMnPO₄ is considered unsuitable for electrocatalytic applications. In order to solve the issue of low conductivity, LiMnPO₄ has been coated or blended with carbon in lithium-ion battery applications [38–43], but these approaches may induce limitations during electrocatalysis via blocking of the active sites or the imperfect contact between LiMnPO₄ and carbon. Further, the synthesis of LiMnPO₄ requires high temperature heat treatments, so these materials are often large and cannot be easily prepared in a supported nanoparticle form [44-46]. As a solution for this problem, we synthesized a LiMnPO₄-carbon composite (LMP-C) by addition of carbon in the initial stage of LiMnPO₄ synthesis, before its formation from the precursors. The as-prepared LMP-C exhibited substantial enhancement in conductivity, which resulted in improved electrochemical properties. An in depth examination of LMP-C was carried out via various X-ray analyses, and the effect of the oxidation state of Mn on ORR activity was also investigated. Based on physical and electrochemical measurements, we verified that LMP-C is a highly active electrocatalyst for ORR, with excellent electrochemical stability even at high potentials and after long-term operation.

2. Experimental

2.1. Preparation of electrocatalysts

 $LiMnPO_4$ catalysts were prepared using a modified solid-state synthesis method [47]. Li_2CO_3 (99%, Aldrich), $MnC_2O_4.H_2O$ (Mn

30% min, Alfa Aesar), H₆NPO₄ (99.999%, Aldrich), and acetone (99.7%, Samchun Chemical) were mixed in a bottle and ball-milled for 24 h in the presence of Ketjenblack (KB) carbon for fabricating LMP-C. For comparison, additional samples were synthesized by the same process but without Li₂CO₃ (to produce a manganese phosphate-carbon composite, MP-C) or without carbon (to yield bare LiMnPO₄; LMP). After the ball-milling process, the samples were sequentially stirred, dried, and ground, Subsequently, the mixed precursors were calcined in a tube furnace at 350 °C for 10 h in Ar, followed by a second heat treatment at 600 °C in an Ar atmosphere for 10 h. For electrochemical measurements, 10 mg of each prepared catalyst was mixed with 30 µL of Nafion ionomer (Aldrich) and 350 µL isopropyl alcohol (Aldrich), and then stirred and further dispersed by ultrasonication to form a catalyst ink. 3.5 µL of ink was deposited on a glassy carbon electrode (geometric area: 0.196 cm²) for the rotating disk electrode (RDE) measurements.

2.2. Materials characterizations

Scanning electron microscopy (SEM, Carl Zeiss AURIGA) images were obtained in order to analyze the bulk structures of the catalysts. Detailed morphologies of the electrocatalysts were characterized by transmission electron microscope (TEM, JEOL JEM-2200) analysis. Sheet resistances were measured by using a 4point probe (CMT-SR1000N, Advanced Instrument Technology). Xray diffraction (XRD) patterns were measured by the Rigaku Dmax 2500 diffractometer with a Cu K α radiation source. X-ray photoelectron spectroscopy (XPS) was performed using SIGMA PROBE (Thermo Fisher Scientific) with an Al K α X-ray source with base pressure of 10⁻¹⁰ Torr.

2.3. Electrochemical measurements

All electrochemical measurements were performed with an Autolab potentiostat (PGSTAT101) using a three-electrode system including a platinum wire counter electrode and Ag/AgCl (saturated KCl) reference electrode. The potentials versus the Ag/AgCl electrode were converted to potentials versus the



Fig. 1. (a-c) SEM images of (a) LMP, (b) LMP-C, and (c) MP-C. (d-g) TEM images of (d,e) LMP and (f,g) LMP-C obtained at (d,f) low and (e,g) high magnifications.

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