The effect of graphene as a support for non-PGM bifunctional oxygen catalyst in rechargeable metal/air batteries

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Graphene, as the rising star in the world of advanced materials, offers game-changing prospects for many key areas of research including energy storage and conversion, biotechnology, novel electronic devices and so forth [1]. Bifunctional oxygen cathodes which can catalyze both ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) are the backbone of rechargeable metal-air batteries as well as regenerative fuel cells [2-4]. Manganese oxides have been vastly employed as a robust cost-effective multifunctional and environmental friendly electrode material in battery industry, from primary to rechargeable metal-air batteries, as well as alkaline fuel cells and capacitors [4]. The electrolytic manganese dioxide (γ-MnO_2) is known as the most electrochemically active crystallographic form of MnO_2 for ORR in alkaline media with Tafel slope of 40 mV dec^{-1} and a low overpotential of -375 mV [2, 5]. However, poor OER electrocatalytic activity of MnO_x in alkaline media diminish the hope of finding an exclusive bi-functional catalyst for both ORR and OER [2]. This could be avoided by adding another class of catalyst active for OER to the MnO_2. $LaCoO_3$, also known as a perovskite-type oxide, has been reported to demonstrate distinguished electrocatalytic activity for OER in alkaline electrolytes in comparison to Pt or MnO_x, i.e. up to 1 mA cm^{-2} at 1600 mV (vs. RHE) as well as a Tafel slope of 60 mV $decade^{-1}$ with excellent durability over 100 cycles in 0.1 M KOH [2, 6]. A thorough comparison with literature regarding other bifunctional electrodes shows that the MnO_2-perovskite catalytic system is very competitive with other catalysts presented in the literature, while having the advantage of cost efficiency and easy preparation methodology [2].

Our research is aimed at investigating the effect support on the performance of MnO_2-based catalysts for both ORR and OER with long cycle life. The mechanisms for OER and ORR of the mixed catalysts and the role of support are investigated by a combination of surface characterization methods and electrochemical techniques.

In the present work, $LaCoO_3$ was synthesized via co-precipitation methods. While different methods for graphene synthesis has been proposed in the literature, a novel approach toward electrochemical exfoliation of graphite assisted by ionic liquids (ILs) was used to synthesize both graphene and N-doped graphene. This approach provides three main features: cost efficiency due to low IL content, extended electrochemical stability in a non-aqueous electrolyte, and high exfoliation yield by effective anionic intercalation within the graphitic layers by IL/acetonitrile electrolyte with dramatically lower loads of ionic liquids (~1:50 IL/acetonitrile vol. ratio) [1]. The catalyst layer consisted of MnO_2:$LaCoO_3$:Support:Nafion with a weight ratio of 1:1:1:0.67. The support varies from the electrochemically synthesized graphene and N-doped graphene to graphitized carbon. Cyclic voltammetry tests were performed in O_2 and N_2 saturated 6 M KOH at

293 K to investigate the electrocatalytic activity of the MnO_2-$LaCoO_3$ catalyst for both OER and ORR on different supports. The longer-term durability of the electrodes was also investigated by performing 100 repeated OER-ORR voltammetric cycles. Combination of Raman and X-ray photoelectron spectroscopy (XPS) as well as SEM analysis were employed to further characterize the catalyst layer.

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