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Effects of testing conditions on the performance of carbon-supported bifunctional electrodes

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ABSTRACT

Carbon-based electrodes with a bifunctional catalyst are being studied extensively for use in rechargeable metal-air batteries. In this study, the effects of various testing conditions on the electrochemical performance, cyclic lifetime, and degradation mechanism of the electrodes prepared using the bifunctional $La_{0.6}Ca_{0.4}CoO_3$ catalyst mixed with the graphitized Vulcan XC-72 carbon black and polytetrafluoroethylene were evaluated in detail. The electrochemical performance and total cycle life of the electrodes were not noticeably affected by the KOH electrolyte concentration or rest time between the charge/discharge. The charge/discharge current density used for the cyclic test significantly influenced both the total cyclic lifetime and degradation mechanism of the electrode. At the higher current densities (± 50 and ± 100 mA/cm^2), carbon corrosion led to electrode flooding and the loss of oxygen reduction capability while the oxygen evolution reaction occurring at the catalyst was largely sustained. At a lower current density (± 6 mA/cm^2), with periodic replacement of electrolyte to avoid carbonate formation in the electrode pores, the loss of the anodic catalytic ability of the bifunctional catalyst presumably via surface oxidation was clearly evident from the increase in oxygen evolution reaction overpotential. With the unchanged electrolyte, the electrode gas transport pore could be blocked by carbonate formation, leading to a decreased catalytic capability of the electrode for oxygen reduction. The failure modes of these electrodes under various cycling conditions were also assessed using impedance spectroscopy and inductively coupled plasma optical emission spectrometry.

1. Introduction

Wind, solar, and tide provide clean and renewable power but their inherent nature as intermittent power sources requires cheap and efficient energy storage devices. Among the choices available, rechargeable metal-air batteries with their high energy storage capacity, low cost, and environment-friendly materials provide one of the most promising solutions [1]. Li-air, Zn-air, Al-air, and Mg-air are some of such aqueous rechargeable metal-air batteries [2,3]. A rechargeable metal-air battery is made up of an anode, cathode, and electrolyte. The lack of durability of the cathode used in a metal-air battery during cyclic charge/discharge operation has been one of the dominant issues and has appropriately attracted enormous research attention [4–7].

Typically, the anodes and cathodes of the rechargeable metal-air batteries are assembled in either a two-electrode or three-electrode design with some exceptions involving a complex five-electrode configuration [8–12]. The three-electrode design has the advantage of allowing the specialized electrocatalysts to perform their respective reactions without exposing them to alternate oxidation or reduction potentials and thus prompting catalyst degradation. In this design, a pair of air electrodes is used for charging and discharging of the battery separately, while the metal anode (e.g., Zn) acts as the third electrode. However, this complex configuration increases the cell volume and decreases the corresponding volumetric energy along with the power density. The requirement of separate electrode housing and electronic controls to switch between the two air electrodes significantly increases both the initial and operating cost of the battery. In a two-electrode design cathode, the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charge are performed cyclically by the same electrode using a bifunctional catalyst that is capable of performing both ORR and OER. Therefore, the development of bifunctional catalysts is extremely challenging and should involve the decrease in both the

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ORR and OER overpotentials without compromising the stability of the catalyst during both the oxidation and reduction cycle.

Noble metal/alloy electrocatalysts exhibit good bifunctional catalytic activities, but are unfavorable mainly for economic reasons [13–16]. The non-noble metal alternatives are perovskites, spinels, and pyrochlores [17–22]. Among them, perovskites with the chemical formula of ABO_3 have been studied extensively due to their high electrochemical performance and chemical stability in the alkaline electrolyte. Ca-doped $LaCoO_3$, especially $La_{0.6}Ca_{0.4}CoO_3$ (LCCO), has so far been the most promising bifunctional catalyst and has been extensively evaluated [23–28]. Several methods such as rotating disk electrode (RDE), rotating ring-disk electrode (RRDE), polarization curves, impedance spectroscopy, cyclic voltammetry, and charge/discharge life cycle test were used to characterize the electrochemical and cyclic lifetime of the proposed catalysts [15,30–33]. Among these, electrodes prepared by dispersing the catalyst on a carbon support and characterization using the polarization curves for electrochemical performance and repeated charge/discharge test for cyclic lifetime are limited [34–38]. Although only a small number of research groups utilize the air electrode with charge/discharge cycle to evaluate bifunctional catalysts, this technique is the best in simulating the conditions experienced by a cathode in a rechargeable metal-air battery.

Variations in both electrochemical performance and cyclic lifetime of similarly LCCO-catalyzed carbon-based electrodes are clearly noticeable in the cyclic lifetime results reported by various research groups [24,25,39,40]. The electrode structure changes drastically with different gas or ion transport channels depending on electrode constituent composition, catalyst, electrode fabrication process, and testing methods employed by these groups. The effects of electrode chemistry like polytetrafluoroethylene (PTFE) content [41] and catalyst composition [42] have been studied to optimize the electrode performance. In addition, the effects of catalyst preparation methods on the performance of the electrode have been documented [39]. Our group investigated the effect of the LCCO catalyst morphology on the performance and stability of the carbon-based electrode [43].

A systematic study regarding the effects of testing conditions on the electrochemical performance, cyclic lifetime, and degradation mechanism of the air electrode is currently lacking. Regarding the electrode degradation during cyclic tests, the deterioration of the catalyst material, corrosion of the carbon support leading to the loss of triple phase boundary (TPB) via excessive electrode flooding [44], carbonate formation in the electrolyte and electrode porous structure [45,46], and the degradation of PTFE [47] are suggested as some of the possible primary degradation mechanisms. The reaction products might affect the electrochemical stability of the electrolyte and consequently the electrode lifetime [48–51]. In addition, the degradation mechanism during cyclic test of similarly catalyzed electrodes appears to be entirely dependent on the testing conditions adopted by different research groups, which is often not addressed or highlighted.

A clear understanding of the role of testing conditions and their effects on both catalyst and cathode degradation are crucial for explicitly comparing the effectiveness of various catalysts reported by different research groups and ascertaining the true catalyst capabilities during cyclic testing. In this study, a graphitized Vulcan XC-72R carbon powder was selected as the support material due to its high resistance to corrosion. The widely used LCCO perovskite is chosen as the catalyst for the electrodes to be evaluated. The objective of this study is two-fold: (i) to assess the effects of various testing conditions on the performance of the bifunctional electrode during cyclic testing and, (ii) to identify the degradation mechanism(s) of the LCCO-catalyzed carbon-based electrode with respect to the cyclic testing conditions based on our work and available literature data.

2. Experimental

2.1. Catalyst, carbon support, and electrode preparation

The LCCO catalysts used in this study were synthesized by the glycine nitrate process and calcined at 650 °C for 2 h in a stagnant air furnace to form the catalyst powder as explained elsewhere [43]. The catalyst powders were then ball milled for 30 min to reduce the particle size. The phase structure, particle size, and morphology of the catalyst powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The carbon support used in this study was the treated Vulcan XC-72R carbon black. It was obtained by graphitizing the as-received Vulcan carbon powder at 2700 °C in an inert environment to improve its corrosion resistance and then heat treating it at 600 °C in air to enable a weight loss of 10% via thermal oxidation for increasing its ORR activity. The surface area of the treated Vulcan powder was 70 m^2/g. The air electrode consisted of a gas diffusion layer, a Ni-mesh current collector, and an active layer. The fabrication procedure for the air electrode was reported elsewhere [43], with the LCCO catalyst loading of 14 mg/cm^2 for the LCCO/carbon electrode. For comparison, a carbon electrode was also prepared using only the treated Vulcan XC-72R carbon black with no LCCO catalyst as reported in Ref. 19.

2.2. Electrochemical testing

The prepared electrodes were tested in a three-electrode arrangement. All measurements were carried out at ambient temperature in air with a 2.85-cm^2 air electrode in a KOH electrolyte with various concentrations (4, 6, and 8.5 M). The KOH electrolyte was not replaced during the cyclic test unless otherwise mentioned. A platinum mesh (4 cm^2) and an Hg/HgO electrode were used as counter and reference electrodes, respectively. The air electrode was placed in the half-cell with the catalyst layer facing the electrolyte and the diffusion side exposed directly to air. The half-cell was maintained at a constant cathodic current density of -100 mA/cm^2 for 1 h followed by -10 mA/cm^2 for 12 h to assure that the electrolyte had sufficient time to penetrate into the structure of the active layer. The polarization curves were then obtained from -0.4 V to 0.7 V vs. the Hg/HgO reference electrode at 3 mV/s and the measurements were compensated for IR-drops using the impedance method suggested by Oelßner et al. [52]. One full cycle of the cyclic test consisted of both cathodic and anodic operation. As shown in Fig. 1, each cycle started with the cathodic operation (i.e., discharge) at a cathodic current density of

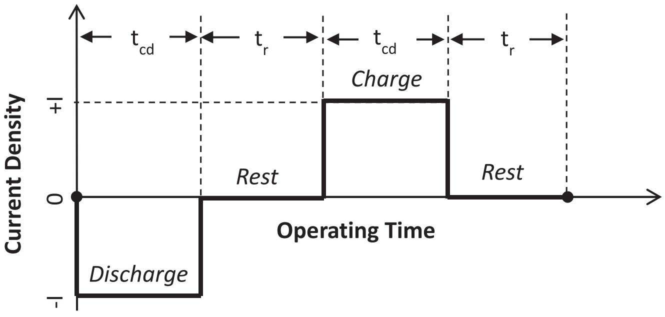

Fig. 1. A schematic showing the current density as a function of the operating time during each cycle used in the cyclic lifetime test for the electrodes. ±I – charge and discharge current density; t_{cd} – charge/discharge time; and t_r – rest time.