



Cycle life limit of carbon-based electrodes for rechargeable metal–air battery application



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ABSTRACT

In this paper, the electrochemical performance and cyclic lifetime of bifunctional electrodes in an alkaline electrolyte were investigated as a function of the perovskite catalyst ($\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ or $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_{3-\delta}$) and the carbon (as-received or graphitized Vulcan XC-72 carbon black). The electrochemical performance of the electrodes was essentially the same, regardless of the carbon and the catalyst; however, the cycle life was directly controlled by the carbon. The graphitized Vulcan-based electrodes had more than twice the cycle life of the as-received Vulcan-based electrodes, due to the better corrosion resistance of the graphitized carbon. The cycle life of the carbon-based electrodes was limited to 100–110 cycles under the testing conditions used in this investigation and the limiting factor was the carbon rather than the catalyst, i.e., the corrosion/oxidation of carbon under the anodic condition. Furthermore, the size/morphology of the catalyst powder affected the electrode performance degradation under cycling noticeably. The failure mechanisms of these electrodes under cycling were also assessed using impedance spectroscopy.

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1. Introduction

A renewed interest in clean and renewable intermittent power sources like wind, solar and tide has sparked a need for better energy storage devices. In theory, rechargeable metal–air batteries with their high energy storage capacity and environment-friendly materials provide one of the most promising solutions [1]. Currently, there are active research efforts in developing various aqueous rechargeable metal–air batteries such as Li–air, Zn–air, Al–air, and Mg–air [2–4]. However, the air electrode of these batteries suffers from poor bifunctional catalytic activity and limited durability/cycle life.

The air electrode of an alkaline rechargeable metal–air battery should be capable of catalyzing both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) and also have a highly porous structure for facilitating oxygen transport. It is generally made of two layers with an inner porous active layer containing bifunctional catalysts in touch with the liquid electrolyte on one side and an outer catalyst-free, water-proofing gas-diffusion layer exposed to air on the other side. A current collector (typically Ni-mesh) is embedded in the outer layer or between the two layers for effective current collection. The hydrophobic outer layer is

typically made of a mixture of polytetrafluoroethylene (PTFE, as a binder) and carbon black with a significant amount of pores. The inner active layer, which is also porous, is composed of carbon support, bifunctional catalyst, and PTFE. Typically, the inner layer has a lower PTFE content than the outer layer to enable better wetting by the electrolyte during operation. The electrochemical performance of the electrode depends on the carbon support, catalyst, internal porosity, and binder content in the active layer. The oxygen reduction takes place near the triple phase boundary (TPB) where the carbon/catalyst, electrolyte and gas are in contact. The life of the electrode depends on the preservation of the delicate wetting properties in the porous electrode structure, as well as the electrochemical stability of the electrolyte and catalyst.

Carbon materials provide notable merits as support, including low cost, wide availability, wettability, large surface areas, high electrical conductivity and good stability in harsh environments. The bifunctional catalysts are usually mixed with finely divided carbon with nanoscale particle size and good dispersion. Different types of carbon with varying structural and physical characteristics have been suggested to improve the electrochemical performance and lifetime of these electrodes [5,6]. Lately, even carbon nanotubes have been employed and shown to greatly influence the performance of the electrodes [7]. However, the carbon support in the active layer is severely attacked by the highly reactive oxygen generated from the OER during charging. Ross et al. [8] demonstrated

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that graphitization of carbon blacks led to a significant reduction in corrosion rate under anodic conditions in alkaline solutions. In spite of these developments, the carbon corrosion is not completely eliminated and the lifetime of air electrode with a carbon-based support is limited [5,9].

To make a sustainable aqueous rechargeable metal–air battery, the development of high-performance bifunctional catalysts is imperative. Noble metal/alloy electrocatalysts exhibit good bi-functional catalytic activities but are unfavorable mainly for economic reasons [10–12]. The non-noble metal alternatives are perovskites, spinels and pyrochlores [13–17]. 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 [17,18]. Ca-doped $LaCoO_3$, especially $La_{0.6}Ca_{0.4}CoO_3$ (LCCO), has so far been the most promising bi-functional catalyst and has been extensively evaluated [5,17,19–21]. The variation in both electrochemical performance and lifetime of the similar LCCO-catalyzed electrode is clearly noticeable among the data reported by different research groups [5,9]. This is mainly due to the various catalyst and electrode preparation methods employed by these groups and consequently a difference in the amount of TPB utilized and the ability of the electrode to maintain these active sites during prolonged charge/discharge cycling. The decomposition of the catalyst material and/or the corrosion of carbon support leading to either the loss of TPB or flooding/mechanical failure of the electrode are suggested as the possible degradation mechanisms. Also, the decomposition products might affect the electrochemical stability of the electrolyte.

In this study, both as-received and graphitized Vulcan XC-72 carbon powders are selected as the support material to further clarify the effects of graphitization on the overall electrode performance and cycle life of the air electrode. The LCCO powder with varying particle morphology/size is chosen as the catalyst for the electrodes to be evaluated. In addition, a $Sr_{0.5}Sm_{0.5}CoO_{3-\delta}$ (SSCO) catalyst with impressive bifunctional activity recently reported by our group is included in the study for comparison [22]. The objective of this study is twofold: (i) to evaluate the electrochemical performance and cycle life of different catalysts with various particle sizes/morphologies mixed with as-received or treated Vulcan carbon black, and (ii) to understand the degradation mechanism(s) of the electrode with respect to both catalyst and support materials under vigorous charge/discharge conditions.

2. Experimental

2.1. Catalyst and carbon support

While the SSCO powder was obtained from Sigma–Aldrich, the LCCO catalysts used in this study were synthesized by the glycine nitrate process (GNP). Aqueous solutions of $La(NO_3)_3$, $Ca(NO_3)_2$, and $Co(NO_3)_2$ (from Alfa Aesar) were prepared separately and mixed in the desired proportions to form a solution with the addition of glycine as fuel. For the LCCO catalyst prepared by the fast GNP process (denoted as LCCO-F), the metal cation-to-glycine molar ratio of 1:1 was utilized; also, the solution was heated at 350 °C, subsequently evaporating the water until it formed a gel that auto-ignited to form ash. For the catalyst prepared by the slow GNP process (denoted as LCCO-S), the metal cation-to-glycine molar ratio was 1:2.25, and the solution was heated at 150 °C while stirring until the water evaporated and then heated to 300 °C to slowly combust into an ash cloud. The collected ash from both processes were ground and then calcined at 650 °C for 2 h in a stagnant air furnace to form the catalyst powder. Some catalyst powders were 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 supports used in this study were as-received and treated Vulcan XC-72R carbon blacks, denoted as Vulcan-A and Vulcan-T, respectively. Vulcan-T was obtained by graphitizing the Vulcan-A powder at 2700 °C 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 the ORR activity [5]. Vulcan-A provides a high surface area of ca. 250 m² g⁻¹, while Vulcan-T has a reduced surface area of only 70 m² g⁻¹.

2.2. Electrode preparation

The air electrode consisted of a gas diffusion layer, a Ni-mesh current collector and an active layer. The hydrophobic diffusion layer preparation started with ball milling a 30 wt% diluted PTFE suspension with 70 wt% acetylene black followed by drying the milled slurry for 12 h at 80 °C. To prepare the semi-hydrophobic active layer, 45 wt% carbon black powder (as-received or treated) and 35 wt% catalyst (SSCO or LCCO) were ultrasonically agitated in excess 2-propanol/H₂O (1:1) followed by mechanical mixing. 20 wt% diluted PTFE suspension was then added into the mixture drop-by-drop while the mixture was being stirred. The agitation–mixing process was repeated once to uniformly disperse the three constituents. The slurry was then filtered and dried for 12 h at 80 °C. Both the dried powders for the active and diffusion layers were kneaded with 2-propanol to form doughs which were rolled in several steps to thin sheets of 0.3 and 0.45 mm, respectively. A 200-mesh Ni current collector was placed between the active and gas diffusion layers, and the assembly was pressed at 340 °C for 30 min under 40 kg cm⁻² to achieve a bonded electrode.

2.3. Electrochemical testing

The prepared electrodes were tested in a three-electrode arrangement. All measurements were carried out at ambient temperature in air with 2.85-cm² air electrodes in an 8.5 M KOH electrolyte. A platinum mesh (2 cm²) and an Hg/HgO electrode were used as counter and reference electrodes, respectively. The 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 rested for 24 h to assure that the electrolyte had sufficient time to penetrate into the structure of the active layer. The polarization curves were then obtained at 3 mV s⁻¹. The measurements were compensated for IR-drops using the impedance method suggested by Oelßner et al. [23]. For the cycle life tests, one full cycle consisted of both processes (0.5 h of cathodic and 0.5 h of anodic operation). The anodic and cathodic current densities used during testing were ±50 mA cm⁻². After each half-cycle, a rest of 0.5 h occurred. The cycle life tests were terminated after the cathodic overpotential reached about –0.3 V. Before and after cycle life testing, the impedance spectra were measured galvanostatically with a Gamry Reference 3000 after the current density had reached a steady state. The frequency range was from 100 kHz to 10 mHz, so that all faradic processes were included.

3. Results and discussion

3.1. Characterization of the catalysts

The XRD patterns for the two catalysts are shown in Fig. 1. Both LCCO-F and LCCO-S powders were single-phase, Fig. 1a and b. The SSCO powder exhibited strong peaks corresponding to a perovskite phase with additional second-phase peaks (identified as $SrCoO_{3-x}$ with a monoclinic structure, ~10 wt%), Fig. 1c.

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