Electrochemistry Communications 75 (2017) 73–77

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Electrodeposited Co-Fe as an oxygen evolution catalyst for rechargeable zinc-air batteries

Ming Xiong, Douglas G. Ivey *

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada

ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form 7 December 2016
Accepted 28 December 2016
Available online 2 January 2017

Keywords:
Oxygen evolution reaction
Co-Fe
Electrodeposition
Zinc-air battery
Nanocubes

ABSTRACT

Cobalt-iron (Co-Fe) nanocubes were directly electrodeposited onto carbon paper and utilized as efficient oxygen evolution reaction catalysts for rechargeable zinc-air batteries. The morphology and mass loading were directly controlled by adjusting deposition time and the deposits evolved from single crystal nanocubes into a continuous film. Co-Fe catalysts exhibited low overpotential, small Tafel slopes and high durability during testing. A zinc-air battery using Co-Fe showed the same cycling efficiency as one using commercial Pt/Ru catalysts.

1. Introduction

Rechargeable zinc-air batteries are promising candidates as grid-scale energy storage devices due to their high theoretical energy density and low cost [1–4]. The efficiency of the discharge-charge cycle is largely dependent on oxygen evolution reaction (OER) catalysts at the air electrode [5,6]. Precious metals like Ru and Ir are two of the most efficient OER catalysts [7], but their scarcity has limited their use for large scale applications. Transition metal-based (Co and Fe) OER catalysts have been developed to replace noble metals, because of their low cost and high stability in alkaline solutions [8–10]. It has been reported that OER activity of Ni or Co-based catalysts can be greatly improved by doping with Fe [11,12]. However, synthesis of these catalysts typically requires complex procedures like hydrothermal methods or high temperature annealing. In addition, conductive additives like carbon black are usually needed to improve the electronic conductivity. Polymer binders like PTFE or Nafion are needed to help combine the catalysts onto the electrode. These steps add extra cost and impair the practicality of the technology. Therefore, it is imperative to find a more efficient way to fabricate and coat catalysts onto the air electrode.

Herein, we use galvanostatic electrodeposition to produce and coat Co-Fe OER catalysts on the air electrode of a zinc-air battery in one step. The electrochemical performance is investigated and compared with commercial Pt/Ru catalysts. Electrodeposited Co-Fe is a body-centered cubic (bcc) solid solution with an oxidized surface that exhibits high catalytic activity for OER and excellent durability in battery environments. The fabrication conditions are easy to control and are scalable.

2. Experimental

2.1. Electrodeposition of Co-Fe on carbon paper

All the reagents were certified ACS grade. The gas diffusion layer (GDL; Teflon-coated porous carbon paper - SGL 35 DC) was used as the substrate for Co-Fe electrodeposition. Electrodeposition was performed in a two-electrode configuration, with GDL (5 cm^2) and Pt mesh as the working electrode and the counter electrode, respectively. Co-Fe was cathodically electrodeposited on the GDL surface in an electrolyte containing $CoSO_4$ (0.15 M), $FeSO_4$ (0.05 M), sodium citrate (0.2 M), boric acid (0.2 M - buffering agent), L-ascorbic acid (0.05 M - antioxidant) and sodium dodecyl sulfate (400 mg L^{-1} - surfactant). A constant current of 150 mA was applied for electrodeposition at room temperature. Samples were rinsed with water after electrodeposition and then dried in air. Mass loading of Co-Fe on GDL was calculated by measuring the weight before and after electrodeposition. Mass loadings of Co-Fe on GDL were 0.2, 0.4, 0.9, 1.7 and 3.2 mg cm^{-2} for 1, 2, 4, 8 and 16 min deposition times, respectively.

2.2. Materials characterization

The structure and composition of the samples were characterized by scanning electron microscopy (SEM; Tescan VEGA3 and Zeiss Sigma) and transmission electron microscopy (TEM; JEOL JEM-2010), along with energy dispersive X-ray (EDX) spectroscopy. The crystal structure

* Corresponding author.
E-mail address: divey@ualberta.ca (D.G. Ivey).

http://dx.doi.org/10.1016/j.elecom.2016.12.018
1388-2481/

was examined using X-ray diffraction (XRD; Rigaku Ultima IV) with Co Kα radiation (λ = 1.789 Å).

2.3. Electrochemical measurements

Linear sweep voltammetry (LSV), chronopotentiometric measurements and cyclic voltammetry (CV) were carried out in 1 M KOH using a potentiostat (Biologic SP-300) with a three-electrode configuration. The Co-Fe coated GDL, Hg/HgO and Pt mesh were used as the working electrode, the reference electrode and the counter electrode, respectively. All potentials in this study are relative to Hg/HgO unless otherwise indicated. All potentials were IR-compensated with the ohmic resistance measured by electrochemical impedance spectroscopy (EIS); typically $R_u = 3–5\ \Omega$. The electrolyte was agitated with a stir bar below the working electrode and the electrolyte was purged with pure O_2 gas to fix the reversible oxygen potential in all experiments [13]. The current densities were normalized to the geometric surface area. The overpotential (η) of OER was calculated from the following equation: η = E(vs. Hg/HgO) – IR – 0.303 V [14]. For comparison, a Pt/Ru catalyst ink was sprayed onto other GDL samples. The ink consisted of 50 mg of Pt/Ru powder (30% Pt and 15% Ru on carbon black, Alfa Aesar) dispersed in 2.0 mL of de-ionized water, 1.0 mL of isopropanol, 0.1 mL of 5 wt% Nafion (D-521) and 0.2 mL of 10 wt% PTFE binder (DISP30). The mass loading of the Pt/Ru ink on GDL was about 1.2 mg cm^{-2} after drying in a furnace.

2.4. Battery testing

Zinc-air battery tests were performed in a home-made cell with the same conditions reported in our previous work [15]. Briefly, Zn foil and the catalyst loaded GDL were used as the anode and the air electrode, respectively. The battery discharge and charge voltages were measured galvanostatically for 10 min at different current densities of 1, 2, 5 and 10 mA cm^{-2}. Discharge-charge cycling was done using a current density of 5 mA cm^{-2} with each cycle consisting of 30 min discharge followed by 30 min charge.

3. Results and discussion

SEM images of Co-Fe catalysts prepared for different deposition times are shown in Fig. 1 (a)–(d). The 1 min deposition sample features cuboidal particles that merge into the porous graphite substrate. The nanocube facets have a terraced structure (inset of Fig. 1 (a)) and a diameter of 100–200 nm. Similar Co-Fe nanocubes have been electrodeposited previously on a flat glassy carbon surface by chronoamperometry, but showed smooth surfaces [16]. The Co-Fe cuboids were further investigated by TEM; one such particle is shown in Fig. 1 (e) attached to carbon from the substrate. A representative selected area electron diffraction (SAED) pattern (inset of Fig. 1 (e)) reveals that each particle is a single crystal and the pattern was indexed to the bcc Co-Fe solid solution. The zone axis is [001], which indicates that the facets are {100} planes. The faint rings in the SAED pattern are from the carbon in the substrate (indexed to graphite). As the deposition time is increased, the Co-Fe nanoparticles grow in size and finally form a continuous film at 8 min (Fig. 1 (b)–(d)).

The crystal structure of the Co-Fe deposits was further studied by XRD (Fig. 1 (f)). For the 1 min deposit, the peak at 52.90° corresponds to the (110) plane of bcc Co-Fe solid solution. The (110) peak shifts to slightly lower angles for longer deposition times, reaching 52.74° for the 4 min and 8 min deposits. A smaller diffraction angle corresponds to a larger d-spacing and lattice parameter. The increase in d-spacing for longer depositions suggests an increase in the amount of Fe, since Fe has a larger atomic radius than Co [17]. The deposit composition can be calculated from the Vegard equation, showing 30.3% of Fe in Co-Fe for the 1 min deposition time and 39.4% of Fe for longer deposition times. EDX spectra also showed a significant oxygen peak providing evidence for oxide formation, which likely occurred during electrodeposition and/or from exposure to the atmosphere after deposition [18–20]. In addition, the anodic process during OER will oxidize Co-Fe. As such, it is the oxidized surface of the Co-Fe particles that provides the active sites to catalyze OER [21,22]. The metal interior provides high electronic conductivity for fast electron transfer between the substrate and surface OER active sites [23].

LSV curves are shown in Fig. 2 (a). The bare GDL substrate has negligible OER activity. However, GDL with electrodeposited Co-Fe has

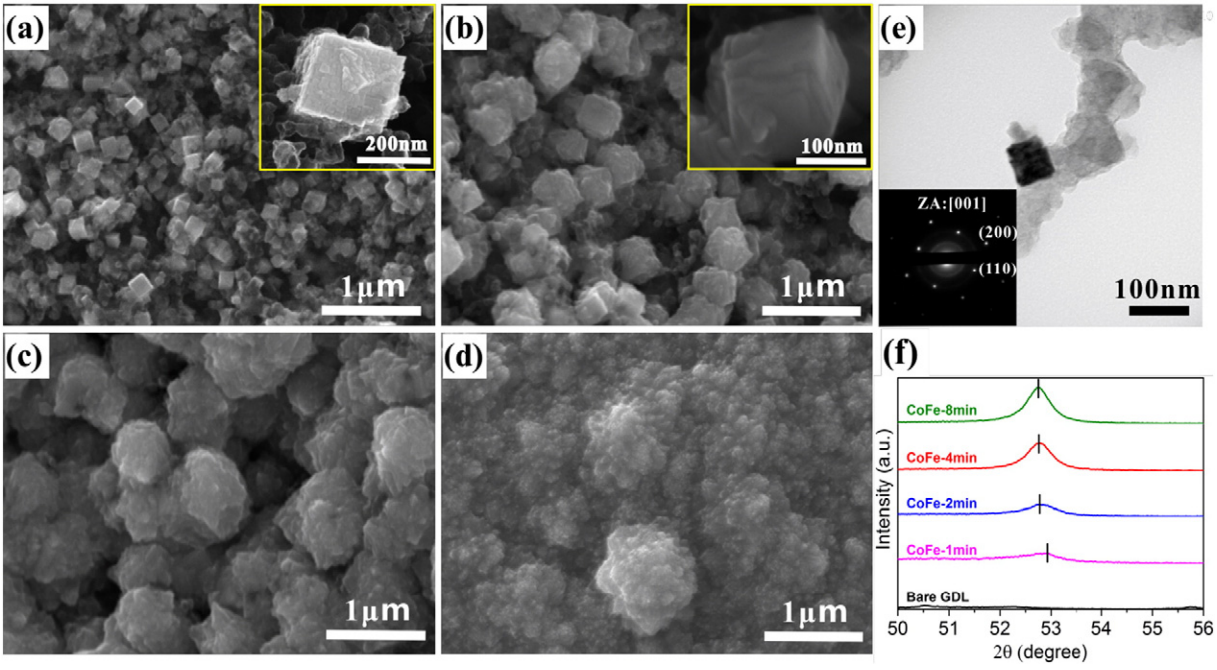

Fig. 1. SEM secondary electron (SE) images of Co-Fe prepared for different deposition times: (a) 1 min, (b) 2 min, (c) 4 min and (d) 8 min. (e) TEM bright field image and diffraction pattern (inset) of Co-Fe after 1 min deposition time. (f) XRD patterns of Co-Fe for different deposition times (magnified pattern).