A Bifunctional Air Electrode Catalyzed by $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ for Zinc-Air Batteries

Xiao-Zi Yuan^a, Wei Qu^{*, a}, Jason Fahlman^a, Douglas G. Ivey^b, Xinge Zhang^a

 ^aNational Research Council of Canada Vancouver, BC, V6T 1W5
^bDept. Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2V4

(BSCF) $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has been recognized as a promising material for ceramic oxygen separation membranes and catalytic membrane reactors due to its outstanding oxygen permeability and high structural and chemical stabilities, combined with interesting catalytic activity for selective oxidation at high temperatures. BSCF has also been recognized as a promising cathode material for IT-SOFCs due to its high surface oxygen exchange kinetics and bulk oxygen diffusion rate at reduced temperatures. More recently, it has been demonstrated that BSCF catalyzes the oxygen evolution reaction (OER) with intrinsic activity that is at least an order of magnitude higher than the state-of-the-art iridium oxide catalyst in alkaline media [1]. It is believed that nanostructured BSCF could further improve its mass activity and thus yield highly efficient OER electrodes. In this work, we report on a bi-functional air electrode using home-made BSCF supported on carbon.

BSCF powder was prepared using a sol-gel method. Analytical grade $Ba(NO_3)_2$, $Sr(NO_3)_2$ Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O and citric acid were used as raw materials. Ammonia water was used to adjust the pH to stabilize the nitrate-citrate sol. The stabilized nitrate-citrate sol was heated slowly to 130°C, upon which a gel like substance was obtained. The final product was then produced by sintering the gel in air at 1000°C for 5 H. The crystal structure of synthesized BSCF was assessed by X-ray diffraction (XRD) with a Bruker D8 advanced diffractometer (Cu $K_{\alpha 1}$ X-ray source, λ = 1.5406 Å) scanned over the range of 10-90° at a scanning rate of 0.1 °s⁻¹. The surface area of synthesized BSCF was examined using a COULTER SA 3100 Series surface area and pore size analyzer (Beckman Coulter, Inc.). The morphology and particle size were observed by transmission electron microscopy (TEM) using a JEOL 2010 instrument operated at 200 kV. The test cell was a self-designed metal-air platform with an active area of 5 cm², which was operated in a two-electrode mode. The working/air electrode was prepared using BSCF contained catalyst ink on a substrate of carbon paper (CP), the reference or counter electrode was Zn and the electrolyte was 6M KOH.

Figure 1 shows an XRD pattern and a TEM bright field (BF) image of the synthesized BSCF. All the observed XRD peaks were indexed to a cubic perovskite structure [2] with a= 0.398 nm, which was confirmed by the electron diffraction patterns obtained from two zone axis orientations (also shown in Figure 1). The BSCF morphology consisted of large plate-like single crystal BSCF particles with <100nm BSCF particles attached. The composition, as determined through EDX analysis of several regions, was close to the target composition of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The BET surface area was 4.99 m²/g with a correlation coefficient of 0.943.



Fig. 1 XRD pattern and TEM BF image of synthesized BSCF. Electron diffraction patterns are also shown



Fig. 2 Cell performance of BSCF air electrode

The best cell performance of the carbon supported BSCF electrode is depicted in Figure 2. The synthesized material exhibited activity for both ORR and OER with ORR activity reaching 83 mA/cm² at a potential of 0.9 V and the OER activity reaching 117 mA/cm² at a potential of 2.2 V at around the 100^{th} cycle. With increasing cycle numbers, both OER and ORR activities had noticeable degradation, especially for the OER (Figure 3).



Fig. 3 Cycling properties of carbon supported BSCF air electrode

In summary, BSCF has superior OER activity and also contributes to the ORR. Therefore, BSCF is very promising for the air cathode of zinc-air batteries. Further performance optimization is still needed to improve its performance and durability.

References

 Jin Suntivich, Kevin J. May, Hubert A. Gasteiger, John B. Goodenough, Yang Shao-Horn, Sciencexpress, 27 October 2011, Science.1212858

[2] Ried et al. J. Electrochem. Soc., 155 (10): B1029-B1035, 2008