

Electrochemical characterization of oxide catalysts by thin film rotating ring disk electrode (RRDE) measurements for application in alkaline energy conversion devices

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The main voltage loss of most electrochemical energy conversion devices, such as anion exchange membrane fuel cells, proton exchange membrane fuel cells or metal/air batteries, is due to the slow kinetics of the positive electrode where the oxygen reduction reaction (ORR) occurs.¹ To date the ORR has been predominantly catalysed by precious metal catalysts in the form of Pt or Pt-based alloys supported on high surface area carbon (Pt/C).² To achieve the same performance for the ORR reducing the noble metal loading, large efforts are currently devoted to search for more active catalysts than state-of-the-art Pt/C, possibly made of non-precious materials. The main advantage of alkaline vs. acidic systems is that a wide range of non-noble metal oxides are stable enough in alkaline media and, thus, many candidates alternative to noble metals can be investigated. Perovskite-type oxides have been recently identified as promising electrocatalysts for the ORR in alkaline media.³ This type of oxide has the general formula ABO_3 where the A site is occupied by an alkaline earth element, such as Ba, Sr, and Ca, and the B site is occupied by a transition metal element in 6-fold coordination to the oxygen atoms.

In this study, two classes of materials have been considered as possible ORR catalysts for alkaline media; a perovskite-type compound ($Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$, BSCF) and a binary oxide with rutile structure (doped SnO_2). A fundamental understanding of the ORR mechanism of these materials in alkaline media has been achieved performing cycling voltammetry and rotating ring disk electrode (RRDE) measurements which allowed evaluating their stability and their activity towards ORR. Particularly, RRDE measurements provided an insight in the ORR mechanism, discriminating between a four or two-electron process.

Both the perovskite and the binary oxide powders were synthesized using a modified sol gel process. Figure 1 shows the X-ray diffraction (XRD) pattern of BSCF oxide powder synthesized by a modified sol gel method described below, and calcined at 1000 °C for 2 h in air. BSCF powder was prepared from an aqueous solution containing Ba, Sr, Co, and Fe nitrate precursors. Citric acid and nitric acid was added to the nitrate solution as a complexing agent and oxidant additive, respectively. The solution was then heated under stirring to evaporate water until it changed into a viscous gel and finally ignited to flame, resulting in a black ash. To obtain single phase material, the BSCF powder was calcined at 1000 °C for 2 h in air. Figure 2 shows a typical scanning electron microscope (SEM) micrograph of the calcined BSCF oxide. For the synthesis of doped tin oxide, chelation of the cations was achieved by adding citric acid to the precursor solution and ethylene glycol was used as polymerization agent. Once a gel was

achieved by heating the precursor solution, it was dried at 150 °C overnight and then calcined at 550 °C for 2 h to obtain single phase material. XRD and SEM characterizations were also carried out for the doped- SnO_2 powder. The specific surface of the oxide catalysts was determined by Brunauer-Emmett-Teller (BET) analysis. The surface area measured for the BSCF was about $10 \text{ m}^2 \text{ g}^{-1}$, while doped- SnO_2 showed higher surface area (about $55 \text{ m}^2 \text{ g}^{-1}$).

For the electrochemical characterization, thin films were prepared by drop-coating a cathode ink on glassy carbon disks. The cathode inks were prepared from a suspension made of 75 mg of oxide (BSCF or doped- SnO_2), 100 μl of Na^+ -exchanged Nafion solution, and 25 ml of isopropanol. In some cases, 15 mg of acetylene black (Alfa Aesar) was added to the cathode ink. The working electrodes were immersed in 0.1M KOH electrolyte saturated with pure Ar at room temperature and the measurements were performed using a hydrogen reference electrode (RHE) and a gold counter electrode in a three electrode configuration. Cyclic voltammetry measurements were carried out to evaluate the oxide catalysts electrochemical stability in different potential windows. RRDE measurements were also performed at room temperature in 0.1M KOH electrolyte, applying different rotation speed and with a scan rate of 5 mV/s.

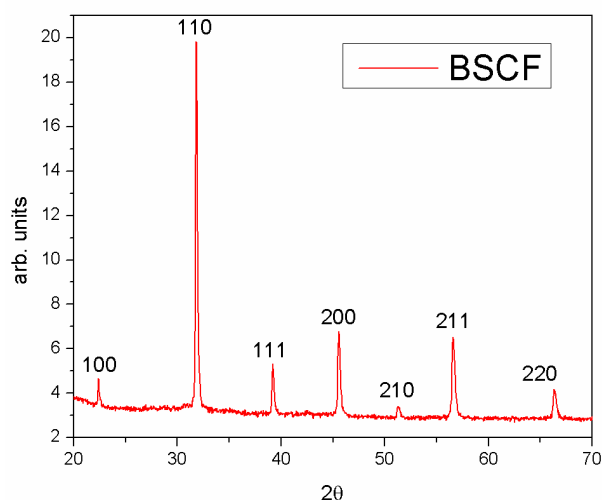


Figure 1: XRD pattern of BSCF powder prepared by a modified sol gel method and calcined at 1000 °C for 2h.

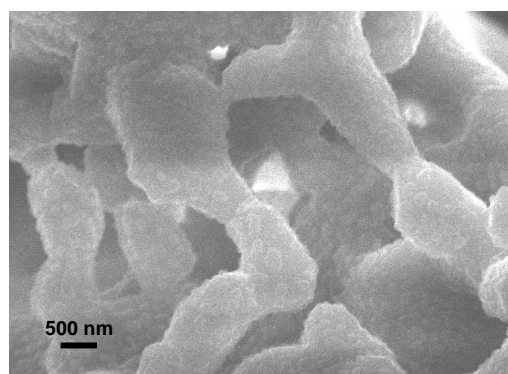


Figure 2: SEM micrograph of BSCF powder calcined at 1000 °C for 2h.

References

- [1] A. Rabis A, P. Rodriguez, T. J. Schmidt, *ACS Catal*, 2 (2012) 864-890.
- [2] M. K. Debe, *Nature*, 7 (2012) 43-51.
- [3] J. Suntivich, H. A. Gasteiger, N. Yabuuchi, H. Nakanishi, J. B. Goodenough, Y. Shao-Horn, *Nature Chemistry*, 2 (2011) 546-550.