

Unraveling the oxygen reduction reaction mechanism and activity of composite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ /carbon electrodes in alkaline media by thin film rotating ring disk electrode measurements

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Alkaline fuel cells (AFCs) were the first low temperature fuel cell developed in the 1960s and mainly used for space program applications [1]. Afterwards, mostly due to the electrolyte deterioration in contact with CO_2 , the interest in these systems has been shelved for many years. However, overcoming the previous limiting drawback of electrolyte carbonization by using an alkaline conductive membrane, the interest in AFCs has risen again in the recent years [2]. Compared to polymer electrolyte fuel cells based on acidic electrolyte membranes, AFCs make use of an electrolyte medium which is less corrosive with respect to a wider range of compounds, thus significantly broadening the range of possible stable and inexpensive electrode materials. Besides the wider range of stable materials, AFCs show the potential of using non-noble electrocatalysts also due the favorable oxygen reduction reaction (ORR) in alkaline media [3]. Due to the above mentioned reasons, a broad range of materials has been investigated in recent years as alternative catalysts to noble metals. Particularly, perovskite oxides have recently showed the potentials of high electrocatalytic activity towards ORR in alkaline media.

The basic perovskite oxide structure can be represented as ABO_3 , where A is the larger cation, such as a lanthanide or an alkaline earth element, and B is the smaller cation, generally a transition metal. The ABO_3 structure can accommodate cation substitution in a wide range by partial substitution of either the A and the B cation with another element giving $(\text{A}_x\text{A}'_{1-x})(\text{B}_y\text{B}'_{1-y})\text{O}_3$ compositions. Most of the perovskite oxides show low surface area, since their synthesis requires relatively high calcination temperatures. Furthermore, they possess relative low conductivity and for this reason carbon is often added to the perovskite electrode to eliminate any possible concern about their electrical conductivity. However, carbon is known to possess a significant activity towards ORR in alkaline media reducing O_2 to peroxide via a two electron process. Therefore, the addition of carbon should be systematically studied in order to verify whether the carbon plays only a simple role of conductive support or if it is actually involved in the ORR kinetics.

In the present work we have investigated the ORR mechanism and activity of composite electrodes made of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF) perovskite and acetylene black carbon by thin film rotating ring disk electrode (RRDE) technique. The RRDE technique allows a fundamental understanding of the ORR mechanism discriminating between a four or a two-electron process. The ratio of BSCF and acetylene black has been systematically varied and the onset potential for ORR and the hydroperoxide formation has been determined for

each composition.

BSCF powders were synthesized using a modified sol gel process, starting from an aqueous solution containing Ba, Sr, Co, and Fe nitrate precursors. Citric acid and nitric acid were 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 $1000\text{ }^\circ\text{C}$ for 2 h in air. The specific surface of the oxide catalysts was determined by Brunauer-Emmett-Teller (BET) analysis. The surface area measured for the BSCF was about $10\text{ m}^2\text{g}^{-1}$. 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 BSCF, Na^+ -exchanged Nafion solution, and acetylene black (Alfa Aesar) in isopropanol. RRDE measurements were performed at room temperature in 0.1M KOH electrolyte, applying different rotation speeds and with a scan rate of 5 mVs^{-1} .

The RRDE measurements showed that composite electrodes possess a more positive onset potential for ORR and a lower hydroperoxide production in the whole tested potential range compared to pure BSCF and acetylene black.

References

- [1] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley, New York, 1992.
- [2] J. R. Varcoe, R. C. T. Slade, *Electrochem. Commun.* 8 (2006) 839.
- [3] G. Merle, M. Wessling, K. Nijmeijer, *Journal of Membrane Science* 377 (2011) 1.