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ENHANCED BIFUNCTIONAL ACTIVITY OF $LaNiO_3$-BASED GAS DIFFUSION ELECTRODES FOR REGENERATIVE FUEL CELLS

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Abstract – **Perovskites are of great interest when searching replacements for precious metals as catalyst for bifunctional oxygen electrodes involving the oxygen evolution (OER) and oxygen reduction reaction (ORR) as is the case of regenerative fuel cells. In this work a full electrochemical study on the electrochemical properties of gas diffusion electrodes (GDEs) using $LaNiO_3$-based catalysts, conducted in alkaline media, led to a study of cyclability and durability. The incorporation of GDEs in a low power electrolyzer/fuel cell prototype was also attempted. The stability of the electrodes was assessed by potential cycling and at constant current density with good results.**

Keywords – **Bifunctional oxygen catalyst; perovskite-type oxides; gas diffusion electrodes; regenerative fuel cells.**

I. INTRODUCTION

RFCs are promising energy storage systems for uninterrupted power supplies, which can provide very high energy storage at minimal weight, by combining an electrolyzer and a fuel cell. Although an appealing technology, their development is still at an early stage. Perovskite-type oxides, with the general formula ABO_3, are potential catalysts for next generation of regenerative fuel cells. Nickel containing perovskite type oxides has been recognised as one of the most promising oxygen electrodes [1]. In this work, a full electrochemical study on the electrochemical properties of gas diffusion electrodes using $LaNiO_3$ based catalyst was carried out. The stability of the electrodes was assessed by potential cycling and at constant current density with good results. Results obtained after incorporation of the compounds in GDE and in low power electrolyzer/fuel cell prototypes are presented.

II. EXPERIMENTAL

Perovskite-type oxide $LaNiO_3$ was prepared by a self-combustion method using citric acid, as previously reported [1]. Structural characterisation was performed by X-ray diffraction (XRD) using a Philips PW 1730 diffractometer, operating with Cu Kα radiation. Electrodes were prepared on carbon paper subtracts, consisting of a diffusion, a catalyst and a Nafion® layer. The GDLs were prepared from carbon black Vulcan XC-72 R, with a loading of 2.5 mg cm^{-2}. To fabricate the catalyst layer, an ink was prepared by suspending the material in isopropanol, and stirring in an ultrasonic bath for 10 min to thoroughly wet and disperse it. A 5% Nafion® dispersion solution (Electrochem, Inc) was then added to the mixture. The catalyst inks were dispersed onto the GDL with a brush, and dried at 50 °C, until a catalyst loading of 5 ± 0.5 mg cm^{-2} was achieved. Finally, a Nafion layer was painted and dried at 50 °C until a loading of 0.7 mg cm^{-2} was reached. The morphology of the oxide electrodes was observed using a Phillips scanning electron microscope, Model XL 30 FEG, coupled to an energy dispersive spectrometer, EDS.

A conventional three-electrode glass cell was used for the electrochemical studies using a PARC model 173 potentiostat. The measurements were carried out at room temperature, using Ag / AgCl / KCl (sat) as the reference electrode to which all potential are referred. A Pt rod was used as counter electrode. A 1M KOH solution was prepared using Millipore Milli-Q ultrapure water. Prior to each electrochemical measurement, the solution was purged with high-purity N_2.

Ageing tests were conducted in two potential ranges: 350 and 650 mV (200 cycles) and an extra 100 cycles between -300 and 700 mV, at a scan rate of 100 mV s^{-1}. In between ageing cycles assessment of stability was done by cyclic voltammetry and electrochemical impedance spectroscopy (EIS), performed using a frequency response analyzer (model 1250, Solartron) connected to an electrochemical interface (model 1286, Solartron). Stability at constant current density (0.4 and 6 mA cm^{-2}), during cycles between the OER and ORR with simultaneous potential monitoring, was assessed.

A 4x4 cm^2 active area PEM electrolyzer/fuel cell (PEM E/FC) was designed and implemented. The structural end plates made