Towards stable bifunctional oxygen electrodes and corrosion resistant gas diffusion layers for regenerative fuel cells

R.A. Silva[1], C.O. Soares[2], M.D. Carvalho[2], M.E. Melo Jorge[2], A. Gomes[2], M.I. da Silva Pereira[2], C.M. Rangel[1*]

[1]*Laboratório Nacional de Energia e Geologia, Paço do Lumiar 22, 1649-038 Lisboa, Portugal*
[2]*C.C.M.M., Departamento de Química e Bioquímica da Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal*

(*) carmen.rangel@lneg.pt

Abstract

Regenerative fuel cells (RFCs) can provide very high energy storage at minimal weight in a dual mode system, by combining an electrolyzer and a fuel cell. Although RFCs are an appealing technology their development is still at an early stage. One key issue is the search for highly active electrocatalysts for both oxygen reduction and water oxidation. Presently, platinum is the best electrocatalyst for the oxygen reduction reaction (ORR), but has a poor oxygen evolution (OER) performance while metal oxides catalyze the OER but not the ORR. Yet, the search for the development of bi-functional oxygen electrodes is also associated to structurally stable gas diffusion layers - they must be capable of withstanding high potentials when cells are operated in the electrolyzer mode and in addition, mass transport limitations when used as a cathode in fuel cell mode.

A novel approach is used in this work to tackle the issue, focussing on the development of stable gas diffusion electrodes for the oxygen reactions, having as a base high surface area $LaNiO_3$. Previous work by the authors has optimised the synthesis of the mentioned perovskite-type oxide, prepared by a self-combustion method. The high electrochemical surface area and low porosity of the oxide has been indicated by electrochemical impedance spectroscopy (EIS) and BET measurements. A full characterization has been the subject of recent publications [1,2].

In a first instance, carbon diffusion electrodes on carbon paper are considered. The gas diffusion layers were prepared from carbon black Vulcan XC-72 R, with a $LaNiO_3$ loading of 3 mg cm^{-2}. To fabricate the catalyst layer, an ink was prepared by suspending $LaNiO_3$ in isopropanol, and stirring in an ultrasonic bath to thoroughly wet and disperses it. A 5% Nafion® dispersion solution (Electrochem, Inc) was then added to the mixture. The catalyst inks were dispersed onto the gas diffusion layer with a brush, and dried at 50ºC, until the desired catalys t loading was achieved. Finally, a Nafion layer was painted and dried at 50ºC. Significant current densities were obtained in both OER and ORR domains. A full electrochemical study was conducted in order to obtain the kinetic parameters in the OER region using a 1 M KOH solution.

Cyclability and stability tests were also conducted. The tests were done in two potential ranges and served as a means of electrode conditioning. The electrode was also subjected to 200 cycles between 0.25 and 0.55 V vs Ag/AgCl (sat.) and an extra 100 cycles between -0.40 and 0.6 V vs Ag/AgCl (sat.), at a scan rate of 100 mV s^{-1}. Additionally a constant current density of ~10 mA cm^{-2} was applied during 50 hours with simultaneous potential monitoring. Activity loss and increasing resistance of the electrodes were observed using cyclic voltammetry and EIS respectively. Carbon oxidation is favorable at the working potentials used which might sets a practical limit on the lifetime of the GDE.

In a second instance, the deposition of $LaNiO_3$ on a Ni foam (1.6 mm thickness, 95% porosity) was effected bringing about more stability in the OER region and Tafel slopes (47 mVdec^{-1}) practically half of the value encountered in the case of carbon paper electrodes. Stability under galvanostatic conditions was assessed at current densities 10 times larger than those used in the case of the carbon paper (100 mA cm^{-2}), also during 50 h, with excellent results. Due to the high stability at anodic potentials found with the Ni foam electrodes and in order to increase current densities, composite electrodes $LaNiO_3$/Pt-Ru were prepared as an alternative to carbon paper electrodes. Results obtained using non-supported Pt-Ru (5-30 wt%) are discussed and compared with the case of carbon-supported Pt-Ru nanoparticles, in the same experimental conditions. It is suggested that $LaNiO_3$ can be used as susbstitute material for carbon black, avoiding the effects of carbon corrosion in the OER region.

Keywords: *perovskite-type oxides, oxygen reactions, gas diffusion electrodes, regenerative fuel cells, platinum*

Acknowledgements: *This work is partially financed by Fundação para a Ciência e Tecnologia (FCT), under contract nº PTDC/CTM/102545/2008. C.O. Soares acknowledges a grant from FCT under the same contract.*

References

[1] C. O. Soares, M. D. Carvalho, M. E. Melo Jorge, A. Gomes, R. A. Silva, C. M. Rangel and M. I. da Silva Pereira. *High Surface Area $LaNiO_3$ Electrodes for Oxygen Electrocatalysis in Alkaline Media*, *J. App.l Electrochem.* 42, pp. 325-332, 2012.

[2] C.O. Soares, R.A. Silva , M.D. Carvalho, M.E. Melo Jorge, A. Gomes, C.M. Rangel, M.I. da Silva Pereira, *Oxide Loading Effect on the Electrochemical Oerformance of $LaNiO_3$ Coatings in Alkaline Media*, *Electrochim. Acta*, 89, pp.106-113, 2013.