Hydrogen insertion in conducting metallic oxides

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Over the last decades, hydrogen in metals, intermetallic compounds and semiconductors have attracted considerable research interest. However, less attention has been paid to hydrogen in oxides, most probably because several oxides are not thermodynamically stable against reduction when they are exposed to hydrogen [1,2]. Recently, attention has been turned toward the use of ruthenium and iridium oxide electrodes as activated cathodes for hydrogen evolution. These oxides show good electrocatalytic activity for hydrogen evolution [3,4,5,6,7,8,9,10,11] and excellent resistance to deactivation due to deposition of metallic impurities [7,12]. They also exhibit an activation (conditioning) period at the beginning where a hysteresis is seen when measuring repeated cathodic polarisation curves with alternate directions of the scan. The overall effect of this activation process is to increase the current density for hydrogen evolution at a fixed electrode potential. Close to a 10-fold increase of the cathodic current has been observed in some cases [11,13]. As suggested elsewhere, part of this effect must arise from an increase of the wettability of the oxide surface as a result of solution spreading over regions made hydrophilic by the reductive treatment [14,15]. However, a comparison of the electrochemically active surface area before and after conditioning by hydrogen discharge shows that the slope of the curve remains between one and two [14,16]. Clearly, there must be some other phenomenon occurring during the oxide activation process.

In this presentation, we will review the behavior of conducting metallic oxides in reductive conditions. Through a series of *in situ* X-ray diffraction measurements, it will be shown that hydrogen absorption occurs in thermally prepared RuO_2 and IrO_2 layer, causing an expansion of the tetragonal unit cell. As evidenced by XPS, these thermally prepared oxide layers do not show any evidence of reduction at their surface. This is in sharp contrast to the behavior of electrochemically produced ruthenium oxy-hydroxide layers that are almost totally reduced to metallic Ru in the same conditions. The reasons underlying this behavior will be discussed.

REFERENCES

1 M. Pourbaix, *Atlas of Electrochemical Equilibria in aqueous solution*, NACE, Houston 1974.
2 S. Trasatti, G. Lodi, in *Electrodes of Conductive Metallic Oxides*, Part A, S. Trasatti, Editor, p. 301, Elsevier, Amsterdam (1980).
3 E. Nicolas, *Eur. Pat. Appl.*, EP 23 368 (1981).
4 J. F. Cairns, D. A. Denton and P. A. Izard, *Eur. Pat. Appl.*, EP 129 374 (1984).
5 A. Nicola, *PCT Int. Appl.*, WO 86 03790 (1986).
6 J. Clerc-Renaud, F. Leroux and D. Ravier, *Eur. Pat. Appl.*, EP 129374 (1987).
7 E. R. Kötz and S. Stucki, *J. Appl. Electrochem.*, 17, 1190 (1987).
8 J. C. F. Boodts and S. Trasatti, *J. Appl. Electrochem.*, 19, 255 (1989).
9 T. C. Wen and C. C. Hu, *J. Electrochem. Soc.*, 139, 2158 (1992).
10 A. Cornell and D. Simonsson, *J. Electrochem. Soc.*, 140, 3123 (1993).
11 M. Blouin and D. Guay, *J. Electrochem. Soc.*, 144, 573 (1997).
12 A. Nidola and R. Schira, *J. Electrochem. Soc.*, 133, 1653 (1986).
13 M. Blouin and D. Guay, in *Electrode Materials and Processes for Energy Conversion and Storage*) PV 94-23, p. 396, The Electrochemical Society Proceedings Series, Pennington, NJ (1994).
14 S. Ardizzone, G. Fregonara and S. Trasatti, *J. Electroanal. Chem.*, 266, 191 (1989).
15 S. Trasatti in *Advances in Electrochemical Science and Engineering*, H. Gerischer and C. W. Tobias, Editors, Vol. 2, p.1, VCH, New York (1992).
16 I. M. Kodintsev and S. Trasatti, *Electrochim Acta*, 39, 1803 (1994).