Anodic deposition of PbO_2/Co_3O_4 composites and their use as electrodes for oxygen evolution reaction

Marco Musiani

Istituto di Polarografia ed Elettrochimica Preparativa del CNR, 4 Corso Stati Uniti, 35127 Padova, Italy

Anodically produced composites in which both the matrix and the dispersed phase are metal oxides (*e.g.* PbO_2/Co_3O_4) are active electrocatalytic materials for the oxygen evolution reaction.

Cathodic deposition of metal–matrix composites is well documented in the literature.[1–5] The composites are obtained by electrolysis of suspensions of electrochemically inert particles in solutions containing electroactive metal cations; when these ions are reduced to form a metal deposit, the particles may become embedded in it. Most composite deposition studies have been aimed at producing metal coatings with special wear resistance or self-lubricating properties,[6] but recently the preparation of electrocatalysts for either hydrogen[7–10] or oxygen evolution reactions[11] has been also pursued with some success. To this aim, the metal matrix (usually Ni) has been modified by electrocatalytic particles (*e.g.* RuO_2).

Anodic deposition of composites is much less known than the cathodic process and in this case the matrix cannot be a metal or an alloy. Both polymer–matrix[12–14] and oxide–matrix[15,16] alloys have been electrochemically produced. In the latter class, PTFE/β-PbO_2 layers were prepared as hydrophobic electrocatalysts for the oxidation of organic molecules.[15,16]

With the aim of producing new electrocatalysts for the oxygen evolution reaction (OER), and possibly other electrochemical oxidation processes, we have investigated the anodic deposition of composites in which a metal oxide of large electronic conductivity is the matrix and an electrocatalytic transition-metal oxide is the dispersed phase. The present work focuses on the synthesis and electrocatalytic properties of PbO_2/Co_3O_4 composites. This system was selected because PbO_2 is an industrially important anode[17] and Co_3O_4 is an active and inexpensive electrocatalytic material.[18] However, many other combinations of matrixes (*e.g.* Tl_2O_3, MnO_2) and dispersed phases (*e.g.* RuO_2, $NiCo_2O_4$) may be obtained in a similar way.

The composite layers were electrodeposited onto Ni rotating disc electrodes at constant current density (typically in the range 1–10 mA cm^{-2}) using a cell with an anode and two cathode compartments. The particles, present only in the anode compartment, were kept in suspension by vigorous stirring. Large Pb sheets were used as cathodes. Two electrodeposition solutions were employed; (*i*) 0.13 mol dm^{-3} $Pb(MeCO_2)_2$ + 0.9 mol dm^{-3} $Pb(NO_3)_2$, pH 4.4 (acid solution) and (*ii*) 0.1 mol dm^{-3} $Pb(MeCO_2)_2$ + 3 mol dm^{-3} NaOH (basic solution). The latter is known to yield α-PbO_2 while either α- or β-PbO_2 is produced from the former depending on current density. The Co_3O_4 particles were *ca.* 1 μm in size. As a general trend, the amount of particles in the composite (evaluated by SEM–EDX analysis) increased by increasing the electrode angular speed ω and the particle concentration in the suspension and by decreasing the current density. A high angular speed also favoured the formation of deposits of homogeneous composition. By electrolysing suspensions with Co_3O_4 volume fraction of 0.0082 at j = 7 mA cm^{-2} and ω = 1500 rpm, deposits with Co_3O_4 volume fractions of 0.14 and 0.09 were obtained from the basic and acid solutions respectively.

Fig. 1(*a*) shows that oxygen evolution from 1 mol dm^{-3} NaOH occurred at markedly less positive potentials on PbO_2/Co_3O_4 composite electrodes than on either PbO_2 or Ni (at j = 100 mA cm^{-2} the potential of the PbO_2/Co_3O_4 composites was *ca.* 300 mV lower than that of Ni). Tafel slopes were 230, 105 and 60 mV $(decade)^{-1}$ for PbO_2 and composites prepared from the acid and basic solutions respectively. Fig. 1(*b*) shows that similar results were obtained in 1 mol dm^{-3} $HClO_4$; again PbO_2/Co_3O_4 composites were better electrode materials than Ni and PbO_2 (at j = 100 mA cm^{-2} the potential of the PbO_2/Co_3O_4 composite electrode prepared from the basic solution was *ca.* 100 mV less positive than that of Ni). The Tafel slopes were lower for composites [105 and 110 mV $(decade)^{-1}$ for those prepared from acid and basic solutions respectively] than for pure PbO_2 [165 mV $(decade)^{-1}$].

In both NaOH and $HClO_4$ media the composites prepared from the basic solution were more active than those prepared from acid solution. As the morphology of both deposits was similar (SEM) and X-ray diffraction showed both composites to

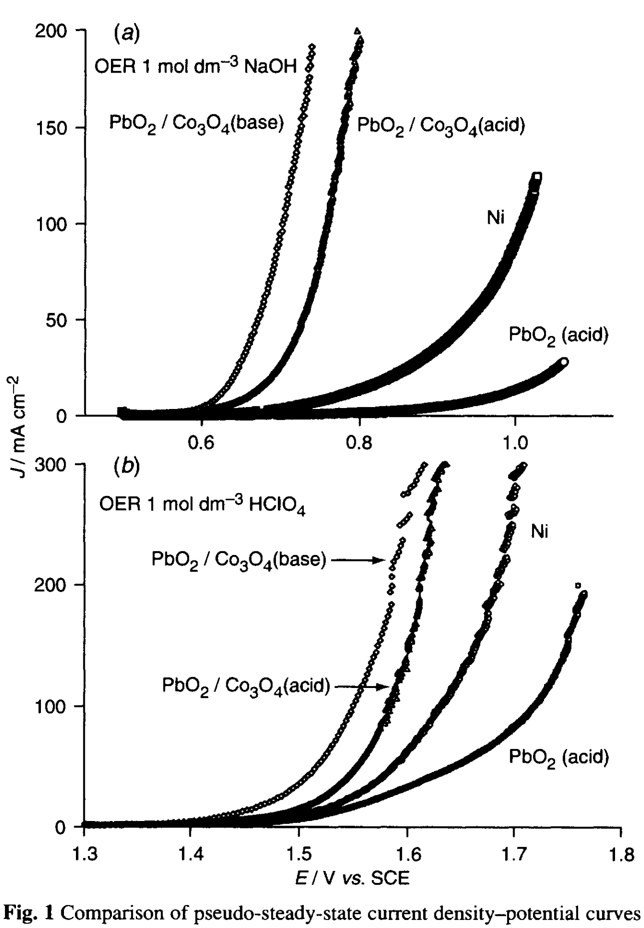

Fig. 1 Comparison of pseudo-steady-state current density–potential curves for OER on Ni, PbO_2 (from acid solution) and PbO_2/Co_3O_4 composites in 1 mol dm^{-3} NaOH (*a*) or 1 mol dm^{-3} $HClO_4$ (*b*). The electrode surface was in a vertical plane; *iR* drop was corrected.

consist of an α-PbO_2 matrix, the higher activity of the former is probably a result of their higher Co_3O_4 content. However, a direct proportionality between OER current densities and Co_3O_4 volume fraction was not observed (surface rather than volume fraction would be more appropriate for attempting normalisation, but such data are not available at this stage). For the composite electrodes prepared from the basic solution, overpotentials for OER at j = 10 mA cm^{-3} were *ca.* 480 mV in 1 mol dm^{-3} NaOH and *ca.* 460 mV in 1 mol dm^{-3} $HClO_4$. At the same current in 1 mol dm^{-3} KOH, overpotentials of Co_3O_4 electrodes prepared by thermal decomposition[19] and spray pyrolysis[20] were 350–450 mV and >550 mV respectively.

When a constant j of 100 mA cm^{-2} was imposed to PbO_2/Co_3O_4 electrodes in an NaOH solution, their potential remained stable for several days. Comparable tests carrier out in $HClO_4$ showed a less steady performance, probably due to the instability of PbO_2.[16,17]

SEM pictures of PbO_2 and PbO_2/Co_3O_4 deposits showed that particle incorporation increased the electrode roughness. Therefore, the marked increase in OER current density obtained with composite electrodes was likely to be the result of both kinetic and geometric factors. However, the change in the Tafel slopes was diagnostic of an authentic electrocatalytic effect by the Co_3O_4 sites.

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References

1 J. R. Roos, J. P. Celis, J. Fransaer and C. Buelens, *J. Met.*, 1990, **42**, 60.
2 J. P. Celis, J. R. Roos, C. Buelens and J. Fransaer, *Trans. Inst. Met. Finish.*, 1991, **69**, 133.
3 C. Buelens, J. Fransaer, J. P. Celis and J. R. Roos, *Bull. Electrochem.*, 1992, **8**, 371.
4 J. Fransaer, J. P. Celis and J. R. Roos, *Met. Finish.*, 1993, **91**, 97.
5 A. Hovestad and L. J. J. Jansen, *J. Appl. Electrochem.*, 1995, **25**, 519.
6 S. Alexandridou, C. Kiparissides, J. Fransaer and J. P. Celis, *Surf. Coat. Technol.*, 1995, **71**, 267.
7 A. Anani, Z. Mao, S. Srinivasan and A. J. Appleby, *J. Appl. Electrochem.*, 1991, **21**, 683.
8 C. Iwakura, N. Furukawa and M. Tanaka, *Electrochim. Acta*, 1992, **37**, 757.
9 . J. Miao and D. L. Piron, *Electrochim. Acta*, 1993, **38**, 1079.
10 A. C. Tavares and S. Trasatti, *GEI 95*, Riccione 24–27 Sept. 1995, Ext. Abs. O13.
11 M. Olesky, A. Budniok, J. Niedbala and P. Matyja, *Electrochim. Acta*, 1994, **39**, 2439.
12 K. Kawai, N. Mihara, S. Kuwabata and H. Yoneyama, *J. Electrochem. Soc.*, 1990, **137**, 1793.
13 F. Beck, M. Dahlhaus and N. Zahedi, *Electrochim. Acta*, 1992, **37**, 1265.
14 F. Beck and M. Dahlhaus, *J. Appl. Electrochem.*, 1993, **23**, 781.
15 A. Yoshiyama, T. Nonaka, M. Sekimoto and Y. Nishiki, *Chem. Lett.*, 1994, 1565.
16 C. N. Ho and B. J. Hwang, *J. Electroanal. Chem.*, 1994, **377**, 177.
17 *The Electrochemistry of Lead*, ed. A. T. Kuhn, Academic Press, London, 1979.
18 S. Trasatti, *Electrochim. Acta*, 1984, **29**, 1503.
19 C. Iwakura, A.Honji and H. Tamura, *Electrochim. Acta*, 1981, **26**, 1319.
20 R. N. Singh, J.-F. Koenig, G.Poillerat and P. Chartier, *J. Electrochem. Soc.*, 1990, **137**, 1408.

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