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Short communication

OXYGEN EVOLUTION ON $La_{0.5}Ba_{0.5}CoO_3$ IN ALKALINE SOLUTIONS

STEADY-STATE AND REACTION ORDER EXPERIMENTS

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INTRODUCTION

In our research into $LaCoO_3$-type compounds we have already studied the reduction of oxygen on electrodes of these materials [1]. Here we will discuss the evolution of oxygen and the dependence of this process on overpotential and hydroxyl ion activity. The $La_{0.5}Ba_{0.5}CoO_3$ used belongs to a class of cobalt-containing oxides that all show good properties as oxygen anode: (La, Ba)CoO_3 and (La, Sr)CoO_3 [2], $NiCo_2O_4$ [3] and Fe/Co_3O_4 [4]. This suggests that in these materials cobalt is the electroactive metal, which is in line with the reported low overpotential of cobalt oxygen anodes with respect to other metal (oxides) in 1 *M* KOH [5].

Regarding the reaction mechanism involved, the Krasil'shchikov path [6] is mainly considered for Ni- and Co-oxides (see e.g. ref. 7) but has the limitation of assumed Langmuir adsorption behaviour of intermediates. Depending on the rate-determining step chosen, this path can lead to a variety of Tafel slopes which, however, are not unique for the Krasil'shchikov scheme. The effects of this path for the Tafel slopes and the reaction order for hydroxide will be discussed.

Since all metal electrodes are at least partially oxidised during oxygen evolution, materials already oxidised are natural candidates for successful use as oxygen electrodes providing that the electronic conductivity and chemical and physical stability are retained. The electronic conductivity of (La, M)CoO_3 with M an alkaline earth element is good (>1 Ω^{-1} cm^{-1}) [8]. (La, Ba)CoO_3 was shown to be chemically stable during oxygen evolution in alkaline solutions at room temperature [2].

EXPERIMENTAL

Cubic perovskite structured $La_{0.5}Ba_{0.5}CoO_3$ was prepared by mixing stoichiometric quantities of La_2O_3, which was prefired at 1200° C for 4 h, $BaCo_3$ and $Co(COOCH_3)_2 \cdot 4\ H_2O$ according to ref. 9. Final samples were obtained by pressing pellets of this material (at approx. 160 MPa) followed by sintering in air or pure oxygen at 1100—1200° C. Absence of foreign phases was checked with X-ray diffraction.

Rotating-disk electrodes (RDE) with geometrical surface areas of about 0.2 cm^2 were made by moulding the pellets in two-component Epofix resin. Contact was made by pressing a platinum wire on to the back of the pellet. The electrode surfaces were ground, polished, qualitatively checked for cracks by optical microscopy and cleaned ultrasonically.

The experiments were carried out at room temperature in a three-compartment Pyrex cell with rotating-disk equipment as described earlier [10].

Electrolyte solutions of different concentration were prepared from analytical grade 85% KOH pellets and twice-distilled water. The hydroxide ion concentration was measured and checked for carbonate contamination using the first derivative of a titration curve obtained with hydrochloric acid, as described by Covington et al. [11].

In the electrochemical cell, the solution was flushed with CO_2-free air.

Hg/HgO/KOH electrodes, based on the design of Thacker [12] and accommodated to each OH^- concentration involved, were used as reference electrodes. Since the dependence of the equilibrium potential on the hydroxide ion activity is the same for the (theoretically) reversible oxygen electrode (ROE) and this reference electrode, the measured potential differences are independent of the hydroxyl activity. From thermodynamic data on the oxidation of Hg one obtains:

$$E(O_2, 1\ \text{atm}) - E(\text{Hg/HgO}) = 303 - (T - 298)\ 0.56\ \text{mV} \quad (1)$$

where T is the temperature in Kelvin. Anodic polarisations were applied potentiostatically, using a slow voltage sweep (0.1—0.01 mV s^{-1}). Measurements were corrected for ohmic resistance of electrode and electrolyte by means of a manual interrupter [13] or an automatic interruptor-compensator [14] based on the method of Britz and Brocke [15].

All overpotentials are given with respect to the ROE. Current densities are calculated on the basis of the geometrical surface area. The electrolyte used was tested colorimetrically for cobalt ions with nitroso-R-salt according to Sandell [16].

RESULTS

Figure 1 shows typical anodic polarization curves for the oxygen evolution on $La_{0.5}Ba_{0.5}CoO_3$ in 3 M KOH at a sweep rate of 0.1 mV s^{-1}. These curves were obtained after stabilizing the electrode at high overpotentials ($\eta > 400$ mV) overnight. After performing a voltage sweep the current always drifted at constant overpotential towards more stable values in such a way that at low overpotentials ($\eta < 200$ mV) the current increased (Fig. 1, curve 2B) while at high overpotentials ($\eta > 300$ mV) the current decreased. The obvious hysteresis was not significantly dependent on the sweep rate between 0.01 and 0.1 mV s^{-1} and was smallest at $\eta \approx 250$ mV. Tafel plots for different electrolyte concentrations and different electrodes are given in Fig. 2. These plots are (logarithmically) averaged for increasing and decreasing potential and show slopes of about 60 mV $decade^{-1}$. Currents measured were independent of the rotation speed for values >70 rad s^{-1}. The dependence of the anodic current on the hydroxyl ion activity for a chosen overpotential is shown in Fig. 3. Current was

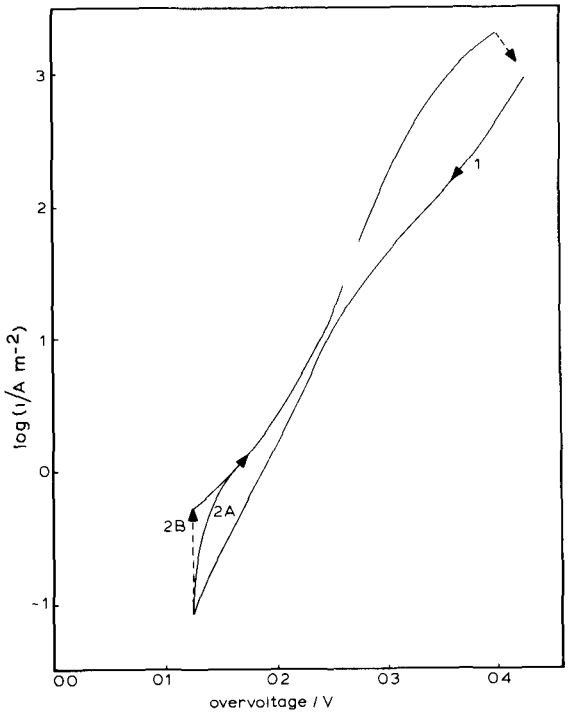

Fig. 1 Current density during a slow voltage sweep on $La_{0.5}Ba_{0.5}CoO_3$ in 3 *M* KOH solution (*iR* corrected). Sweep rate 0.1 mV s^{-1}. (1) Decreasing sweep after stabilizing at high potential, (2A) continuing increasing sweep without halt at low potential, (2B) increasing sweep after halt at low potential.

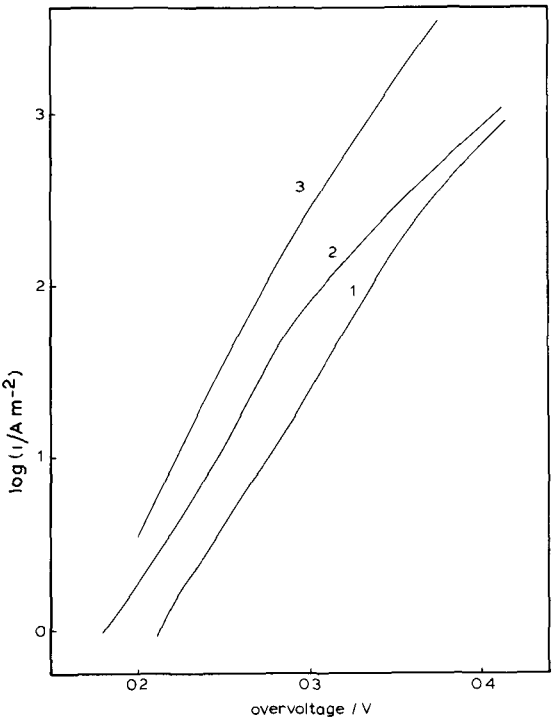

Fig. 2. Averaged current density responses for different hydroxyl concentrations and different electrodes. Sweep rate 0.1 mV s^{-1} (*iR* corrected) (1) 1 5 *M* KOH, $a(OH^-)$ = 1.1 mol l^{-1}, electrode I; (2) 3 *M* KOH, $a(OH^-)$ = 3 mol l^{-1}, electrode I, (3) 7.5 *M* KOH, $a(OH^-)$ = 25 mol l^{-1}, electrode II.

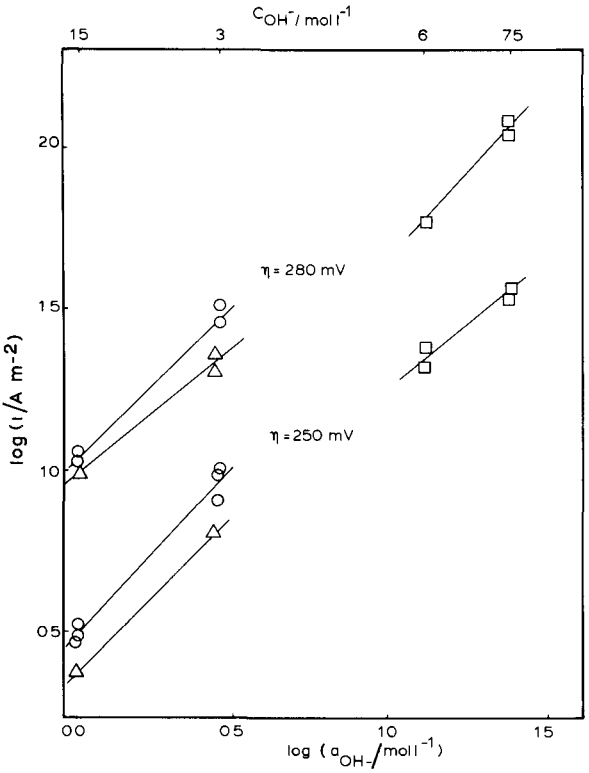

Fig 3 Dependence of the current density on the hydroxyl ion activity, measured at η = 250 mV and η = 280 mV for different electrodes. (△) electrode III; (□) electrode II; (○) electrode I

measured for three electrodes with slightly different geometrical surface areas at η = 250 mV during decreasing potential sweeps, after stabilizing at high overpotential for about 16 h. The activity of the KOH solutions was calculated from the measured molarity and the appropriate activity coefficients as given by Akerlof and Bender [17]. The carbonate content of the electrolyte used was found to be <1%. No dissolved cobalt species could be detected in the electrolyte used after test periods of up to one week, in which a total charge of approximately 10^4 C passed the electrode. Since the measured detection limit in our case was ≈1 ppm, corrosion of the materials in terms of dissolution is negligible (<1 μg h^{-1}). However, other corrosion effects might still be active (see Discussion below).

DISCUSSION

The current—voltage characteristics measured in 6 *M* KOH solution are similar to earlier results [2]. The Tafel slopes of about 60 mV decade^{-1} are in fair agreement with our earlier values and with the results of Honji et al. [4] for Fe supported Co_3O_4, but also with the values for $NiCo_2O_4$, erroneously

published by Jasem and Tseung [3] as 33 mV, which should actually be 2.3 times as large.

The anodic current density on oxygen evolution is proportional to the hydroxyl ion activity, as follows from the slopes of the $\log(i)_\eta$ vs $\log a_{OH^-}$ plots of Fig. 3, which vary between 0.8 and 1.1. For the measurements an overpotential of 250 and 280 mV was chosen, because around these values the averaged Tafel plots, as well as the separate current responses for increasing and decreasing potential show reasonable straight lines with slopes of about 60 mV decade^{-1} and display only minor hysteresis. Any effects other than Nernstain of changing electrolyte activity on the electrode potential (diffuse double-layer effects) can be neglected because of the high bulk ion activity used. Effects of mass transport and electromigration may also be ignored in our present experimental conditions. From the results obtained the anodic current density can be described by

$$i = k\, a_{OH^-} \exp(\eta F/RT) \qquad (2)$$

As can be seen from the discussion of possible oxygen evolution mechanisms, e.g. by Riddiford [18], many mechanisms can result in a Tafel slope of 60 mV decade^{-1}. An OH^- reaction order of 1 at constant overpotential is possible only for a chemical rate-determining step involving hydroxide ion, for instance step (2) in the Krasil'shchikov mechanism [6] at low coverage of the OH radicals:

(1) $OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OH_{ad} + e$

(2) $OH^- + OH_{ad} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O^-_{ad} + H_2O$

(3) $O^-_{ad} \rightleftharpoons O_{ad} + e$

(4) $2\, O_{ad} \rightarrow O_2$

This scheme was also given by Miles and Huang [7] for the oxygen evolution on different metal oxide electrodes in alkaline solution. An equivalent mechanism for IrO_2 in acid solution was proposed by Gottesfeld and Srinivasan [19].

So if we assume the Krasil'shchikov path to apply in this case, the second step is rate determining, as found earlier on the basis of Tafel values and reaction order by Kas'yan et al. [20] for the evolution of oxygen on a nickel electrode in alkaline solutions.

At present the observed hysteresis cannot be explained, but it might point to a parasitical corrosion process at high overpotentials, leading to an effective partial blocking of the electrode surface.

CONCLUSIONS

The results of the kinetic experiments may be explained with the Krasil'shchikov mechanism by taking the second step as rate determining and assuming low coverage Langmuir adsorption. If we drop this condition and tolerate interaction of adsorbed intermediates by switching to Frumkin-type adsorption, it is

not yet clear whether the same mechanism and rate-determining step can still account for the obtained experimental facts. This and the observed non-stationary behaviour necessitate further investigations.

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