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Electrocatalytic activity and stability of $La_{1-x}Ca_xCoO_3$ perovskite-type oxides in alkaline medium

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Abstract

Electrocatalytic activity versus oxygen evolution of perovskite-type cobalt oxide ($La_{1-x}Ca_xCoO_3$, with $x = 0.0$, 0.2, 0.4 and 0.6) was evaluated by potentiostatic polarization technique, as a function of the electrode chemical composition. Stability of the electrode material in alkaline medium under stressing galvanostatic conditions was investigated. Highly sensitive differential pulse adsorptive stripping voltammetry (DPAdSV) technique was successfully applied for determination of traces of dissolved cobalt in the electrolyte solution. The results point out the optimum electrode activity and stability of the $x = 0.4$ composition.

Keywords: Perovskite-type cobalt oxide; Electrocatalytic activity; Stability; Differential pulse adsorptive stripping voltammetry

1. Introduction

Electrochemical evolution and reduction of oxygen in alkaline medium are of considerable interest [1,2]. They are most important processes in many electrochemical devices such as metal–air batteries [3], fuel cells [4] and water electrolyzers [5]. Numerous oxygen electrodes have been investigated and extensively reviewed. Among these, perovskite-type oxides of lanthanum and cobalt appear to be promising as air electrodes for both the evolution [6] and the reduction [7] of oxygen, and can thus be used simultaneously as bi-functional electrodes [4]. Cobaltate compounds ($La_{1-x}Me_xCoO_3$, Me = Ca or Sr), in which calcium or strontium are partially substituted for lanthanum, have shown interesting high electrical conductivity because of their partially filled σ* band [8], which also produces high electrocatalytic activity versus oxygen evolution reaction [9].

Electrode stability is one of the most important features and is often the decisive parameter for the choice of an electrode structure. Although very slight anodic dissolution of cobaltate electrodes, occurring at high current densities ($\geq 25\,mA\,cm^{-2}$), has been reported in [9], their unaltered conductivity and electrocatalytic properties make them extremely useful as anode materials in alkaline solutions.

Because of the high stability constant and specific interaction of dimethylglyoxime ($DMGH_2$) with cobalt and nickel, the development by Nürnberg and coworkers [10,11] of differential pulse adsorptive stripping voltammetry (DPAdSV) led to the determination of these metals in the adsorbed $[Me(DMGH)_2]^{2+}$ complex form. This method, which has become a standard procedure, has been employed to determine cobalt traces as dimethylglyoximates with a detection limit of 10^{-10} M [12,13]. Detailed electrochemical and spectroscopic studies on the reduction process observed at mercury hanging electrode are all consistent with an overall 10 electron reduction process, in which both the $DMGH_2$ ligand and cobalt ions are reduced in the adsorbed state [14]:

$$Co^{2+} + 2DMGH_2 \rightarrow [Co(DMGH)_2]^{2+} + 2H^+ \quad \text{(solution)} \tag{1}$$

$$[Co(DMGH)_2]^{2+} + Hg \rightarrow [Co(DMGH)_2]^{2+}_{ads}Hg \quad \text{(electrode)} \tag{2}$$

$$[Co(DMGH)_2]^{2+}_{ads}Hg + 10e^- + 10H^+ \rightarrow Co(Hg) + 2[2,3\text{-bis(hydroxylamino)-butane}] \tag{3}$$

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with $DMGH_2$ and 2,3-bis(hydroxylamino)-butane compounds having the $C_4H_8O_2N_2$ and $C_4H_{12}O_2N_2$ chemical formulas, respectively.

The object of the present work is to study the electrocatalytic properties and stability of a perovskite-type $La_{1-x}Ca_xCoO_3$ series towards oxygen evolution in alkaline medium, and to investigate the applicability of the aforementioned method to the determination of slightly dissolved cobalt(II) in the working medium.

2. Experimental

Perovskite-type cobalt oxides $La_{1-x}Ca_xCoO_3$ ($x = 0.0$, 0.2, 0.4 and 0.6) were synthesized following the so-called amorphous citrate method [15]. Highly pure commercial grade reagents were used. The required stoichiometric amounts of metal nitrates ($La(NO_3)_3{\cdot}6H_2O$; Prolabo, purity ≥99.9%, $Co(NO_3)_2{\cdot}6H_2O$; Prolabo, ≥99.9% and $Ca(NO_3)_2{\cdot}4H_2O$; Aldrich, ≥99.99%) and dehydrated citric acid ($C_6O_7H_8$, ≥99.9%) were dissolved in 500 ml of 1-propanol (C_3H_5OH, ≥99.5%). The solvent was evaporated from the homogeneous solution until a gel was obtained. The dried gel, leading to a solid precursor, was annealed in air at 700 °C to yield a black powder of electrocatalyst. Electrodes of 1 cm^2 were obtained by pressing into pellet form an accurate weight of 0.35 g of powder for 5 min at 7 t cm^{-2}.

To perform electrochemical experiments, potassium hydroxide electrolyte solution (1 M) was prepared by dissolving the required amount of KOH (Merck, ≥99.99%) into bi-distilled water. For Co determination, the pH of the alkaline solution was adjusted by means of supra-pure concentrated hydrochloric acid (Matthey, ≥99.999%). An amount of 0.1 M sodium chloride (Strem, ≥99.999%) and $DMGH_2$ (Lancastre, ≥99%) were added as supporting electrolyte and complexing agent, respectively. Standard solutions of cobalt, containing also NaCl and $DMGH_2$, were prepared by direct dilution from a stock solution of cobalt(II) (Aldrich, 995 μg/ml) to the required concentrations.

Electrochemical measurements, which included current–overpotential and potential–time curves, were carried out using a PJT 120-1 Tacussel potentiostat–galvanostat and a PE 8116 Y-t Sefram recorder. A bright platinum (2 cm^2) foil and an Hg/HgO/1 M KOH electrode were used as counter and reference electrodes, respectively. For the sake of comparison, a platinum foil (1 cm^2) was also tested as working electrode. The cell was a single-compartment Pyrex glass containing 50 ml of 1 M KOH electrolyte.

DPAdSV technique was performed on computerized electrochemical potentiostat (EG & G Princeton Applied Research, model 263 A), interfaced with a PAR model 303 stand (SMDE) and a PAR model 305 stirrer. Electrodes, placed in a polarographic cell, consisted in this case of a hanging mercury medium size drop working electrode (HMDE), a platinum wire as counter electrode and an Ag/AgCl/saturated KCl reference electrode. A PHN81 Tacussel pH-meter was used for pH measurement. All experiments were carried out at a temperature of 25 °C.

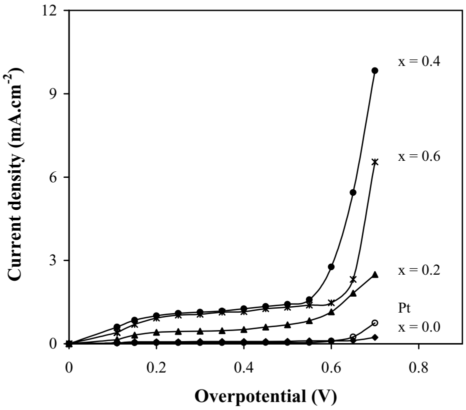

Fig. 1. Current–polarization curves of oxygen evolution on $La_{1-x}Ca_xCoO_3$ electrodes in 1 M KOH at 25 °C (current densities are based on geometric surface areas).

3. Results and discussion

3.1. Electrocatalytic activity

Oxygen evolution reaction from KOH solution ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$), operating as a principal process in alkaline water electrolyzer, is taken as the test reaction. Fig. 1 shows the anodic current–overpotential curves of the different $La_{1-x}Ca_xCoO_3$ electrocatalysts. The electrode materials with large x values (i.e. $x = 0.4$ and 0.6) exhibit higher anodic activity than those with smaller x values. Compared to the $x = 0.6$ and Pt electrodes, the $La_{0.6}Ca_{0.4}CoO_3$ one appears to be much more active. The effect of the substitution ratio x on the electrode kinetics was clearly established in a previous study [15]; it was accredited to the evolution of the electrode active surface area (i.e. the electrode/electrolyte interface at which the reaction takes place) with x. Actually, when the parameter x varies from 0 to 0.6, both of the electrode surface area (examined by scanning electron microscopy and estimated by the BET method on powders) and the electrode activity exhibit a clear-cut parallel trend, passing by their respective maximum values at $x = 0.4$.

3.2. Stability tests

The estimation of the lifetime of electrodes under real operational conditions requires extremely long experiments. However, on a laboratory scale such a parameter may be evaluated by means of accelerated tests which consist, for instance, to subject the electrodes to intensive anodic or cathodic discharges and analyze the behavior of the electrode

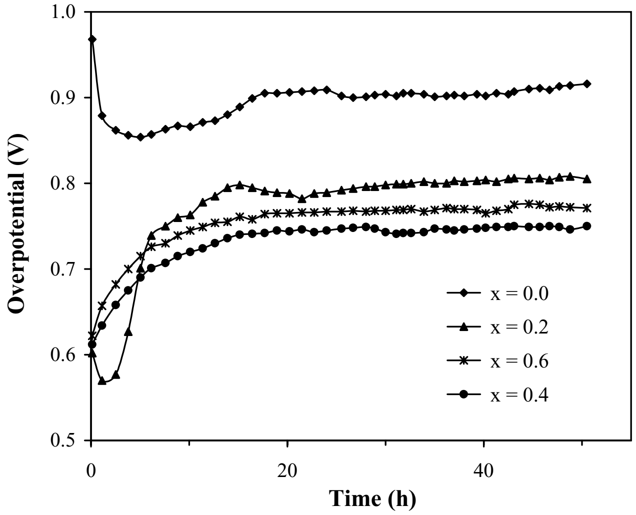

Fig. 2. Overpotential–time curves of $La_{1-x}Ca_xCoO_3$ electrodes under 25 mA cm^{-2} anodic current in 1 M KOH at 25 °C.

potential. Stability of $La_{1-x}Ca_xCoO_3$ active anodes was examined by polarizing the electrodes at a relatively high, constant current density of 25 mA cm^{-2} in the same alkaline solution and continuing O_2 evolution for a period of 50 h. The variations of the electrode potential with time during the anodic polarization are illustrated in Fig. 2. The plots recorded on the substituted electrodes show that the potential rises gradually during the first stage (15 h) and then stabilizes, affording a first evidence of the electrodes stability under these stressing conditions. It is noteworthy that the electrode with $x = 0.4$ shows the lowest overpotential, in accordance with its greatest electroactivity manifested through the current–overpotential characteristics (see Fig. 1).

According to Matsumoto et al. [9], anodic dissolution of $La_{1-x}Ca_xCoO_3$, based on thermodynamic data of cobalt [16], occurs likely according to

$$La_{1-x}Ca_xCoO_3 + (1-3x)OH^- + H_2O \rightarrow CoO_2 + (1-x)La(OH)_3 + xCa^{2+} + (1-x)e^- \quad (4)$$

CoO_2, being unstable in solutions with pH greater than 10, decomposes subsequently into $HCoO_2{}^-$ ions as follows:

$$CoO_2 + OH^- \rightarrow HCoO_2{}^- + \tfrac{1}{2}O_2 \quad (5)$$

3.3. Dosage of dissolved cobalt

At the end of each polarization test, the electrode was removed and the amount of cobalt, possibly dissolved in the electrolyte solution, was determined. For this purpose, 10 ml of each electrolyzing solution, adjusted at different pH, or of standard solutions were pipetted into the polarographic cell, to which NaCl and $DMGH_2$ were added. The new solution was mixed thoroughly and deaerated with pure argon (grade 6.0) for 4 min. The adsorption potential (E_{ads}) was fixed at −0.8 V versus Ag/AgCl. The dissolved cobalt, determined as a surface active $[Co(DMGH)_2]^{2+}$ complex, was accumulated onto the mercury working electrode for 2 min under a constant stirring. Subsequently, the stirring was turned off. The potential was scanned cathodically within the −0.8 to −1.2 V versus Ag/AgCl potential range with a scan rate of 2 mV s^{-1}.

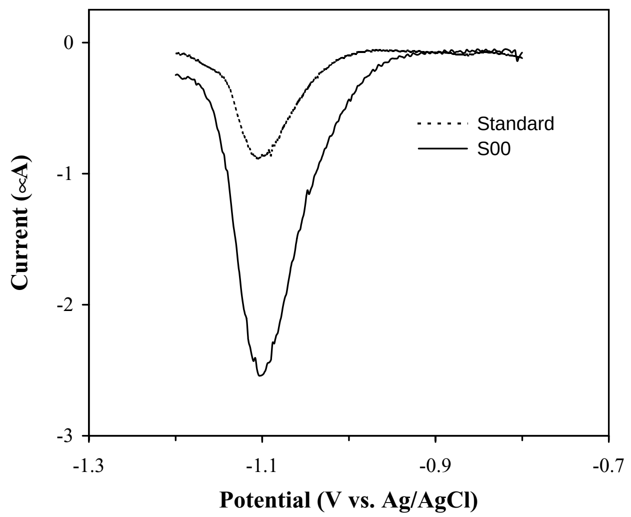

Fig. 3. Differential pulse polarograms of Co^{2+} in a standard solution (—) of 10^{-5} M Co^{2+}, containing 2×10^{-5} M $DMGH_2$ and 10^{-1} M NaCl, and in solution S00 (- - -) containing 10^{-4} M $DMGH_2$ and 10^{-1} M NaCl (pH 6, $E_{ads} = -0.8$ V, $t_{ads} = 2$ min, $v = 2$ mV s^{-1}, $T = 25$ °C).

The solution samples analyzed are hereafter denoted as S00, S02, S04 and S06 with reference to solutions in which electrodes with compositions x = 0.0, 0.2, 0.4 and 0.6, respectively, were polarized. Fig. 3 illustrates typical differential pulse voltammograms of a standard solution and solution S00 at pH 6. Well-defined cobalt signals at −1.1 V versus Ag/AgCl are observed. These signals are in good agreement with the literature data [17,18], indicating that the cathodic reduction, according to Eq. (3), of adsorbed $[Co(DMGH)_2]^{2+}_{ads}$ complex on the HMDE was achieved. It should be noted that an electrolyte solution which was not electrolyzed gave a plot with no significant current in the explored potential range, indicating that the detected cobalt ions stem from the tested electrode materials.

pH of the medium is an important factor influencing the stability of the complex and thereby the peak height [18]. Its influence on the voltammograms was studied on solution S00 over the 13.8–1 pH interval by adding concentrated HCl solution to the polarographic cell, keeping other variables constant. Observations were that while the peak current I_p was strongly affected by pH variations, the shape of the corresponding voltammograms was found to be nearly unchanged over the whole pH domain. The peak potential E_p was insensitive to pH changes, contrary to what was stated by Puri et al. [19], reporting a shift towards more negative potential values. Fig. 4 shows that the peak current is small over the 13.8–10 pH range, due to the instability of cobalt complexes [20]. The peak height, however, increases

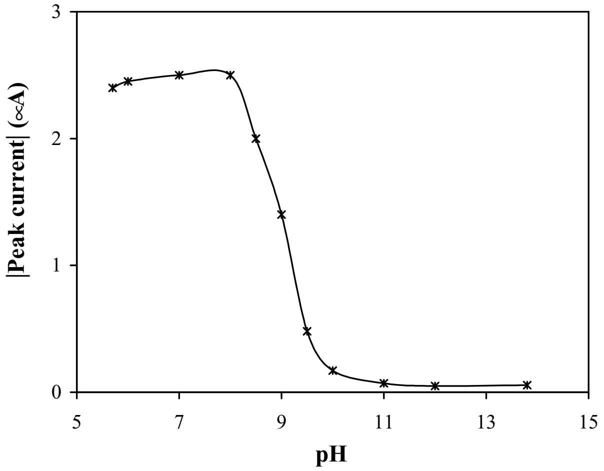

Fig. 4. Dependence of peak height I_p on pH of solution S00, containing 10^{-4} M DMGH$_2$ and 10^{-1} M NaCl (pH 6, $E_{ads} = -0.8$ V, $t_{ads} = 2$ min, $v = 2$ mV s^{-1}, $T = 25\,^{\circ}$C).

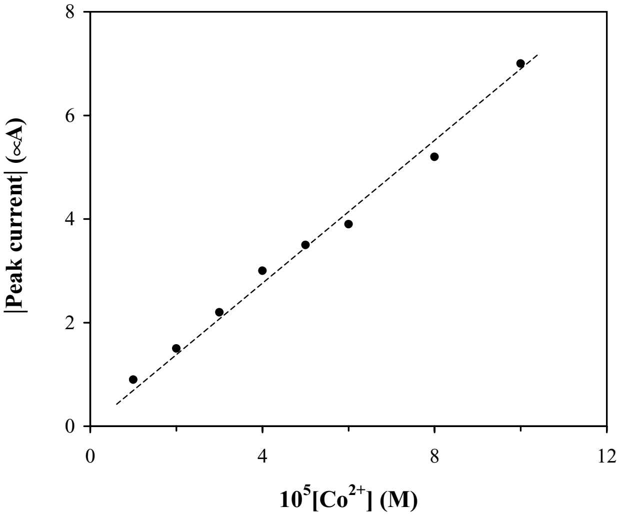

Fig. 5. Calibration plot I_p–Co^{2+} concentration (pH 6, $E_{ads} = -0.8$ V, $t_{ads} = 2$ min, $v = 2$ mV s^{-1}, $T = 25\,^{\circ}$C).

gradually as the pH decreases below 10 as a consequence of greater production of Co^{2+} species, resulting from the following reaction:

$$HCoO_2^- + H_2O \rightarrow Co^{2+} + 3OH^- \quad (6)$$

which, in presence of DMGH$_2$, are subsequently complexed, adsorbed and then reduced, according to steps 1–3. The peak current reaches its maximum between pH 8 and 5.7. If the pH is less than 5.7, the peaks of [Co(DMGH)$_2$]$^{2+}$ complex reduction, whose values are not represented on the I_p–pH plot, are completely suppressed and voltammograms show waves. The adsorption of the complex at the electrode surface is obviously inhibited. This phenomenon seems to be attributed to H$^+$ ions competing with the complex adsorption [19].

The calibration plot between the peak current I_p and the concentration c of cobalt was obtained by testing standard solutions for various concentration levels. The I_p value represents an average of three determinations with each tested solution. As shown in Fig. 5, the current increases linearly over a range of 10^{-5} to 10^{-6} M Co^{2+}, with increasing cobalt concentration, with a correlation factor of 0.99.

The amounts of dissolved cobalt in solutions S00, S02, S04, and S06 were quantified using the calibration plot and the DPAdSV peaks illustrated in Fig. 6. The Co concentrations are given in Table 1. The results show that the amounts are very low, reflecting the quite good stability of the electrode materials under the test conditions. Interestingly, the smaller dissolved Co^{2+} concentration values are obtained with the $x = 0.4$ and 0.6 electrodes, which also exhibit the higher electroactivity. It is then clear that the presence of calcium has a stabilizing effect on the oxide lattice. In a previous investigation of the La$_{1-x}$Ca$_x$CoO$_3$ system, we stated that numerous physicochemical features (i.e. Co^{4+}/Co^{3+} ratio, unit cell parameters, particle morphology, specific surface area, etc.) were dependent on the substitution ratio x, explicitly showing optimum performances with $x = 0.4$ composition. Definitely, if the results of these accelerated stability tests reproduce reliably those of the prolonged operational conditions, the numerous virtues demonstrated for

Table 1
Determination of dissolved cobalt in solutions S00, S02, S04 and S06

Solution	Concentration of Co^{2+} (M)
S00	3.5×10^{-5}
S02	3.2×10^{-5}
S04	6.0×10^{-6}
S06	4.0×10^{-6}

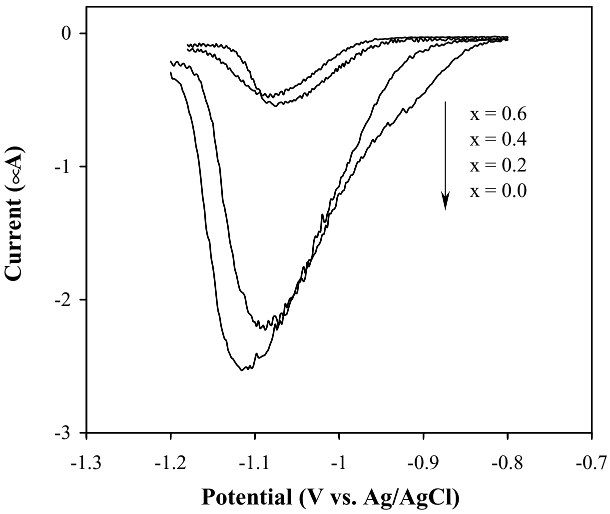

Fig. 6. Differential pulse voltammograms of Co^{2+} in solutions S00, S02, S04, and S06 (pH 6, $E_{ads} = -0.8$ V, $t_{ads} = 2$ min, $v = 2$ mV s^{-1}, $T = 25\,^{\circ}$C).

this composition make it unrivaled anode material for oxygen evolution in alkaline solutions.

4. Conclusion

This work was undertaken in order to look into the electrocatalytic activity and stability of $La_{1-x}Ca_xCoO_3$ oxygen electrodes as a function of the substitution ratio. Anodic polarization experiments showed that the electroactivity of $La_{0.6}Ca_{0.4}CoO_3$ electrode was the highest among the compositions examined. DPAdSV technique has been successfully applied for the detection of dissolved cobalt induced by limited electrode degradation. This determination was optimal between pH 5.7 and 8. Tiny amounts of dissolved cobalt evaluated by this sensitive method confirm the quite good stability of the electrode materials under anodic polarization in alkaline medium within the test period. In this respect, $La_{0.6}Ca_{0.4}CoO_3$, allying excellent electrocatalytic activity and good stability, appears to be a promising material for the anode in commercial electrolysis cells. The work is being completed by further tests to assess its long-term stability at high current densities.

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