



Surface characterization of $\text{LaNiO}_3/\text{Ni-PVC}$ composite

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Abstract

The perovskite LaNiO_3 was prepared by the sol-gel method. Electrodes of $\text{LaNiO}_3/\text{Ni-PVC}$ were obtained by painting a conductive Ni-PVC composite substrate with a suspension of the LaNiO_3 powder in an ethanol-tetrahydrofuran mixture. They were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and energy dispersive spectroscopy (EDS). The study of the electrochemical response of this composite was performed in alkaline solutions by cyclic voltammetry, open circuit potential and by voltammetric charges. The state of the surface and the contribution of the Ni-PVC substrate in the electrochemical behavior of LaNiO_3 were studied for the same electrode after prolonged repetitive potential cycling and oxygen evolution. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the activity and stability of electrocatalysts; the catalyst surface plays an important role. However when the catalyst, for example spinels and perovskites, is supported on a collector surface, the properties and the behavior of the catalyst [1,2] can be affected by the bulk characteristics and the structure of the substrate [2,3].

During the last number of years the sol-gel method was employed for preparation of transition metal mixed oxides, both spinel structure and perovskite structure types. The preparation of spinels and perovskites by a sol-gel route [4] leads to high specific area powders [5–8] with reasonable activity. In particular LaNiO_3 was synthesized via the sol-gel process using maleic acid [5,9] and propionic acid [5] as complexing agents.

The reported electrocatalytic activity in relation to oxygen evolution in KOH solutions deals with pellets of these microcrystalline and ultrafine electrocatalyst particles, painted layers or thin films on conductive supports. However the principal problem of these electrodes can be the electrocatalyst adherence on the substrate and erosion of surface with continuous use. Long-term experiments have been reported to manifest time invariance of the electrode potential [5,9–11] but the possibility of the anodic dissolution of the LaNiO_3 catalyst and the contribution of the substrate in the evolution of the service life have not been sufficiently investigated. In view of this, this paper reports the electrochemical characterization of the LaNiO_3 perovskite on the Ni-PVC composite; the influence of the Ni-PVC substrate on the behavior of the LaNiO_3 catalyst and on the electrocatalytic activity for the oxygen evolution reaction. For the composite $\text{LaNiO}_3/\text{Ni-PVC}$ differing in the nature of the reported sub-

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strates [5,9,11–14], the study of the effect of electrochemical aging on the composition and the structure of the surface layers represent interesting tasks.

2. Experimental

2.1. Preparation of LaNiO_3 and $\text{LaNiO}_3/\text{Ni-PVC}$ samples

Perovskite was prepared via the propionic acid sol-gel type route as reported in the literature [5] and was calcinated at 850 or 900°C over 2.5 h in the presence of air.

The Ni-PVC composite substrate was prepared following the procedure described elsewhere [2,15]. Electrodes $\text{LaNiO}_3/\text{Ni-PVC}$ were made painting a Ni-PVC substrate with a suspension of the catalyst oxide in a tetrahydrofuran-ethanol mixture (2:98 by volume), resulting in film electrodes of about 2 μm thick. The $\text{LaNiO}_3/\text{Ni-PVC}$ and LaNiO_3 samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The XRD patterns were obtained with a Siemens D 5000 diffractometer by using Cu-K_α radiation (35 kV, 30 mA) at 2 different scan speeds (1 and $0.5 \times 2\theta^\circ \cdot \text{min}^{-1}$). Interpretation of critical lines was achieved with the help of the fitting profile program of Socobim-Siemens. SEM micrographs and EDS analysis was carried out by means of a JSM 5400 microscope equipped with a microprobe Voyager Noran system.

An ohmic contact was made to one side of the Ni-PVC electrode by means of a conducting silver epoxy resin (Demetron) with a nickel wire embedded in the resin, which was used to isolate the no working surface. The apparent surface area used as electrode was ca. 0.2 cm^2 .

2.2. Electrochemical measurements

Electrochemical studies were carried out in a polypropylene cell and the counter electrode was a Pt foil (ca. 5 cm^2). Potentials were measured against the Hg/HgO reference electrode in the same electrolyte solution. All the experiments were carried out at 25°C, in deaired 1 or 5 M KOH (Merck). The electrochemical measurements were made using a potentiostat-galvanostat UAP/LODZ.

The electrochemically active surface area of the fresh electrodes was determined from double charge curves using a cycling voltammetry technique [16]. The roughness factor was calculated by assuming a double-layer capacitance of 60 $\mu\text{m} \text{cm}^{-2}$ for a smooth oxide surface. As surface concentration of the active sites participating in the surface redox reaction during the use of the

$\text{LaNiO}_3/\text{Ni-PVC}$ electrodes we used the voltammetric charge between 0 and 0.55 or 0.64 V at 50 $\text{mV} \cdot \text{s}^{-1}$.

The steady state polarization curves in 1 or 5 M KOH for the oxygen evolution reaction were obtained for fresh and aged electrodes, in the potential range from 0.5 to 0.9 V versus Hg/HgO. The current-voltage curves were not corrected for iR drop.

3. Results and discussion

3.1. Characterization of LaNiO_3 and $\text{LaNiO}_3/\text{Ni-PVC}$

Recently, Chartier et al. [5] have reported on the preparation of the pure LaNiO_3 phase by calcination at different temperatures/times of 850°C/6 h and 900°C/6 h in the presence of air of the resulting gel from the propionic acid sol-gel. However when the perovskite powder was synthesized via the same propionic acid sol-gel process and calcinated also at 850°C or 900°C, but no more than 2.5 h in the presence of air, the X-ray analysis showed that the LaNiO_3 in reality consisted of LaNiO_3 , NiLa_2O_4 and NiO, as a mixed multiphase (Fig. 1, diffractogram (a)). The corresponding unit cell parameters were: $a = 5.445 \text{ \AA}$, $c = 6.578 \text{ \AA}$ with $c/a = 1.208$ for LaNiO_3 ; and $a = 3.823 \text{ \AA}$, $c = 12.680 \text{ \AA}$ with $c/a = 3.3167$ for NiLa_2O_4 . These cell parameters present less than 1% deviation from those reported by JCPDS-ICDD (ASTM): $a = 5.457 \text{ \AA}$, $c = 6.572 \text{ \AA}$ (for

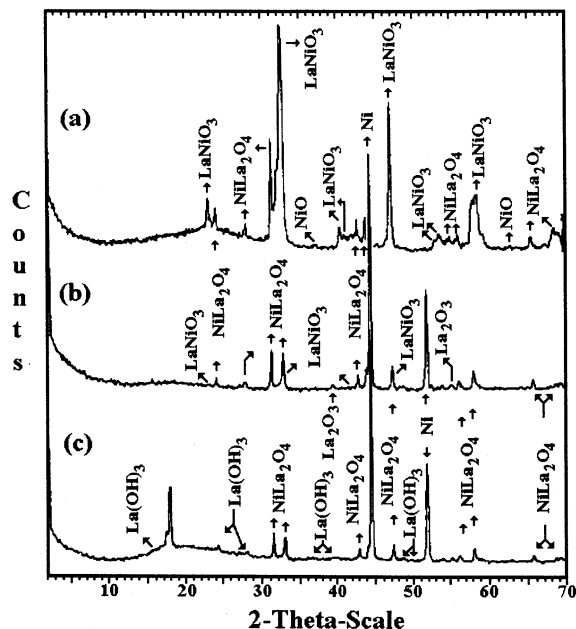


Fig. 1. X-ray diffractograms for LaNiO_3 synthesized via the propionic acid sol-gel process, 850°C/2.3 h/air (a) and after prolonged repetitive potential cycling and anodic polarization in 1 M KOH (b) and 5 M KOH (c).

Table 1
Multiphase composition of different samples

Sample	NiLaO ₃ (%)	NiLa ₂ O ₄ (%)	NiO (%)	Other (%)
NiLaO ₃ powder	65	30	5	
NiLaO ₃ /Ni-PVC film after electrochemical aging in 1 M KOH	5	15	75	
NiLaO ₃ /Ni-PVC film after electrochemical aging in 5 M KOH	5	10	60	5 La(OH) ₃

LaNiO₃) and $a = 3.855 \text{ \AA}$, $c = 12.652 \text{ \AA}$ (for NiLa₂O₄). After prolonged cycling and anodic polarization at 0.9 V in 5 M KOH (Fig. 1, diffractogram (c)) the unit cell parameters for LaNiO₃ ($a = 5.430 \text{ \AA}$, $c = 6.578 \text{ \AA}$) and NiLa₂O₄ ($a = 3.822 \text{ \AA}$, $c = 12.68 \text{ \AA}$) did not show appreciable change, while NiO presented a slight deviation from the ASTM value ($a = 4.176 \text{ \AA}$) with the magnitude $a = 4.22 \text{ \AA}$. Nevertheless the surface composition of LaNiO₃/Ni-PVC is altered after electrochemical treatment as it could be evaluated after comparison of the diffractograms in Fig. 1 as discussed below.

The approximated proportion of the compounds in the mixed multiphase were calculated using the intensity of their corresponding maxima and are shown in Table 1. We could observe a diminution of the NiLaO₃ and NiLa₂O₄ content after the electrochemical experiments. Moreover, 5% La(OH)₃ was formed, together with 20% of the component appearing at the $18^\circ 2\theta$ value. Although the amount of some components in the mixed multiphase was small, the calculated cell parameters are close to the values reported by ASTM.

The scanning electron micrographs of LaNiO₃ powder and films of LaNiO₃ obtained on the Ni-PVC composite substrate are shown in Fig. 2(a and b). In both micrographs, poorly shaped, almost isometric agglomerates of the particles with a size of about 0.1 μm are observed. No alteration is observed on the morphology of the LaNiO₃ after painting one side of the Ni-PVC support with a slurry containing the LaNiO₃, tetrahydrofuran and ethanol. The etching of the PVC polymer by the solvent during the painting of the Ni-PVC substrate, served to fix the catalyst particles on the substrate. The analysis of EDS spectra (Fig. 3) for LaNiO₃ powder (a), LaNiO₃/Ni-PVC (b) and Ni-PVC (c) showed the presence of the PVC (as chlorine) in the LaNiO₃/Ni-PVC sample.

3.2. Electrochemical behavior of LaNiO₃/Ni-PVC

For characterization of the electrochemical behavior of LaNiO₃/Ni-PVC electrodes in alkaline solutions, cyclic voltammograms were run within the potential region between 0 versus Hg/HgO and oxygen evolution reaction (OER). The performance of the LaNiO₃/Ni-PVC electrode in alkaline solution 1 M KOH between 0 and 0.64 V or 0 and 0.55 V for 5 M KOH was

investigated. Fig. 4 shows the cyclic voltammogram of the LaNiO₃/Ni-PVC electrode in 1 M KOH at 50 mV s⁻¹. In this voltammogram the characteristic anodic and cathodic peaks located at 0.595 V versus Hg/HgO and 0.275 V versus Hg/HgO, corresponding to the redox couple Ni(III)/Ni(II) can be observed.

When comparing the anodic and cathodic peaks potential reported by Chartier et al. [5] for LaNiO₃/Ni foil, with the obtained by us under the same conditions, one observes a shift in the anodic and cathodic peaks of 90 and 31 mV, respectively. At the same time, the

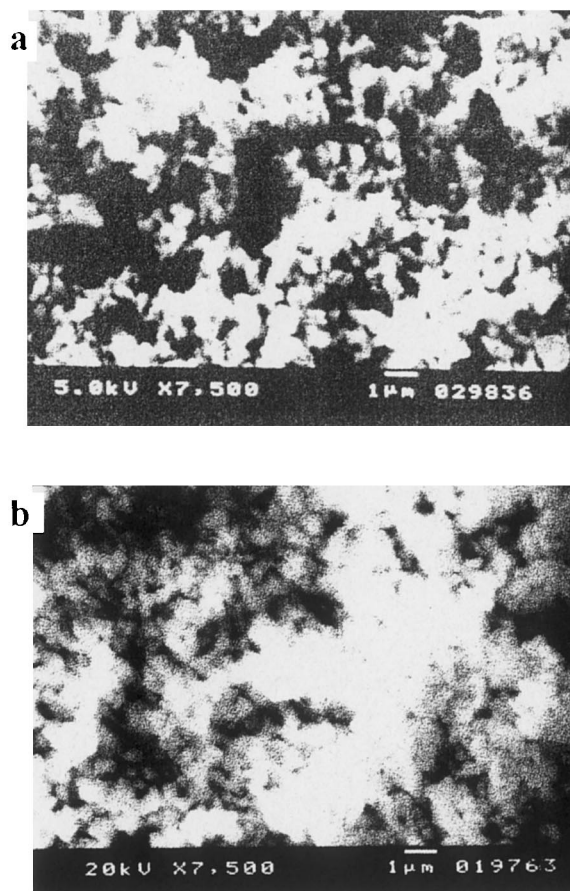


Fig. 2. SEM micrograph top view for LaNiO₃ powder prepared via the propionic acid sol-gel process (a) and freshly prepared LaNiO₃/Ni-PVC electrode (b).

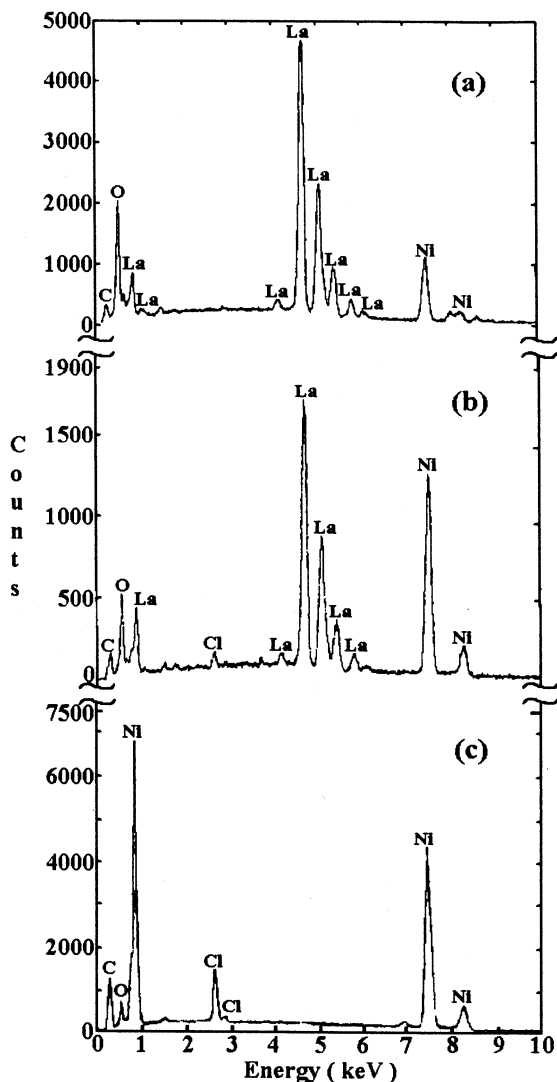


Fig. 3. EDS spectra of LaNiO_3 powder prepared via the propionic acid sol-gel process (a), of LaNiO_3 layers applied on PVC (b) and for the Ni-PVC substrate (c).

apparent current densities are three times greater on $\text{LaNiO}_3/\text{Ni-PVC}$. The effect of the morphology on the peak potential position for the LaNiO_3 obtained by spray pyrolysis on Pt foil has been previously reported by Singh et al. [14]. In our case the presence of PVC among the LaNiO_3 grains, together with the surface morphology can produce these shifts.

These peaks and their corresponding charges are affected by repetitive potential steps. The stabilization of the voltammetric response was obtained after prolonged cycling. After 40 min cycling, the cathodic charge variation is very small (Fig. 4 inset). On the stabilized $\text{LaNiO}_3/\text{Ni-PVC}$ electrode the effect of scan rate on the anodic and cathodic peaks was examined

(Fig. 5). It was observed that the peak potentials always shift farther apart with increasing scan rate. The peak currents were found to vary linearly with the square root of the scan rate (Fig. 6), showing that the redox processes are diffusion controlled.

The roughness factor of the $\text{LaNiO}_3/\text{Ni-PVC}$ electrodes was estimated utilizing cyclic voltammetry (Fig. 7) and the plots of current charge versus sweep rate (Fig. 8). The values of the roughness factor for fresh $\text{LaNiO}_3/\text{Ni-PVC}$ electrodes were 16 for 1 M KOH and 33 for 5 M KOH. These roughness values are smaller in comparison with those reported by other authors in the case of pellets [5,9], films of this perovskite on Ni foil [5] or Pt foil [12], in which no binding agents were used in the electrodes preparation step. However, such electrodes can be unstable for practical applications. In case of $\text{LaNiO}_3/\text{Ni-PVC}$ composite, the adherence and mechanical properties are very good and the amount of electroactive perovskite material employed for electrodes preparation is small. The last made these electrodes attractive.

The low and different values of the roughness factor in 1 M and 5 M KOH can be due to the PVC films removed during the painting of the substrate and blocking a different fraction of the pores and of the electroactive centers of the perovskite. The existence of insulating films of PVC around and between aggregates of LaNiO_3 particles decreases the active electrode surface, leaving only a determined amount of LaNiO_3 sites exposed to the electrolyte.

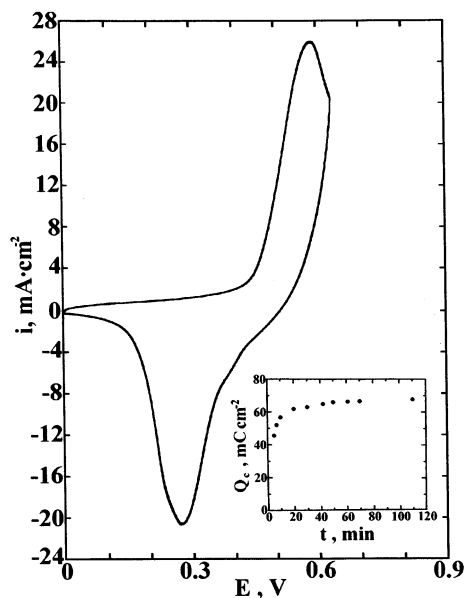


Fig. 4. Voltammetric curve at $50 \text{ mV}\cdot\text{s}^{-1}$ in 1 M KOH solution for the fresh $\text{LaNiO}_3/\text{Ni-PVC}$ electrode. Inset: variation of the cathodic charge with cycling time for the same electrode.

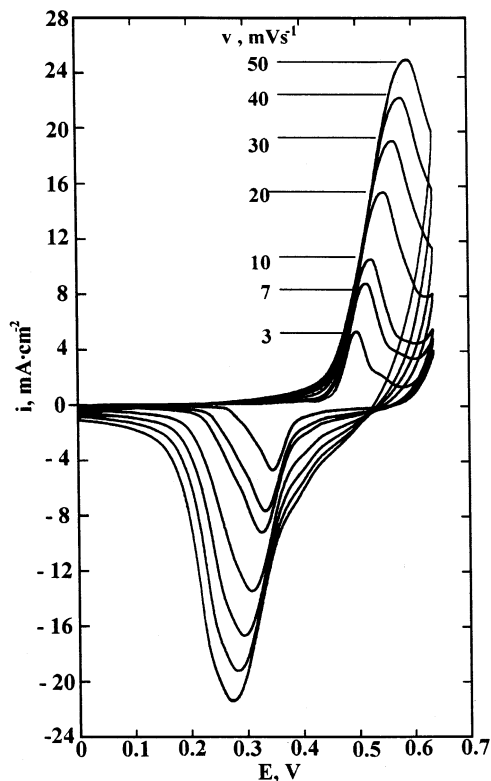


Fig. 5. Voltammograms of the stabilized LaNiO₃/Ni-PVC electrode in 1 M KOH at different scan rates.

3.3. Inner and outer active surface

The SEM study (Fig. 2b) shows that the fresh LaNiO₃ layer on Ni-PVC is formed by particles separated by highly defective regions. This suggests that the interfaces oxide/solution macroboundaries (outer surface), oxide/solution microboundaries, due to penetration of the electrolyte into pores and intercrystallite regions (inner surface) and into the oxide layer/support interface should be considered.

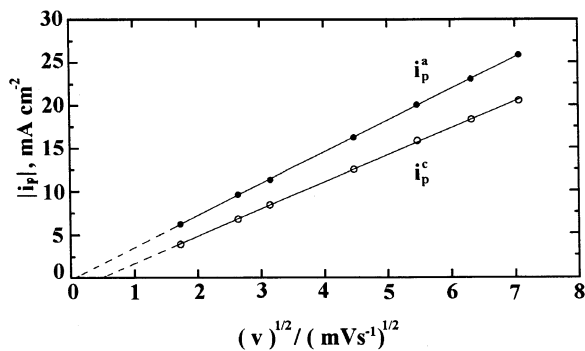


Fig. 6. Variation of anodic and cathodic peak currents as a function of the square root of the scan rate for LaNiO₃/Ni-PVC in 1 M KOH at 25°C.

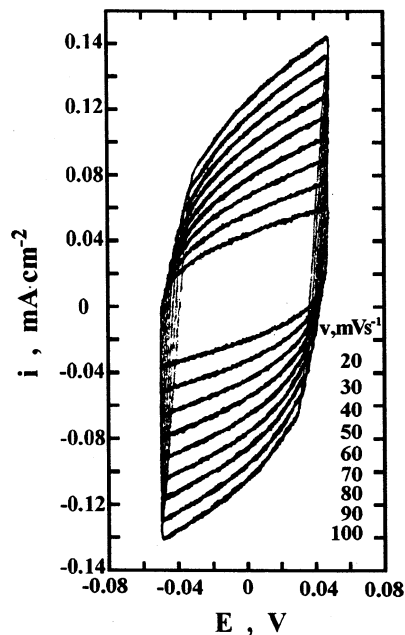


Fig. 7. Cyclic voltammograms of the interface LaNiO₃/Ni-PVC film in 1 M KOH at different scan rates in the potential interval ± 0.05 V versus Hg/HgO.

For the stabilized LaNiO₃/Ni-PVC electrode in 1 M and 5 M KOH it was observed that the voltammetric charge q decreases as the potential scan rate v is increased. This can be attributed to difficulties for proton exchange along pores, crack and grain boundaries [17]. Employing the extrapolation procedure of the $1/q$ versus $v^{1/2}$ and q versus $v^{-1/2}$ curves (Fig. 9) discussed by Trasatti and coworkers [18–20], an attempt to separate the inner surface charge from the outer surface charge was made (Table 2). Here we can observe that the electrochemical pretreatment by repetitive potential cycling ensures effective utilization of the internal surface area of the LaNiO₃/Ni-PVC electrodes. The high value of the ratio q_i/q_T in alkaline solutions after prolonged

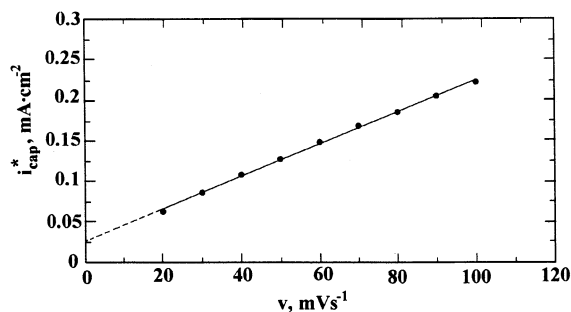


Fig. 8. Capacity current against scan rate plots for the LaNiO₃ layer on Ni-PVC in 1 M KOH at 25°C.

Table 2
Effect of cycling on roughness, outer and inner surface of LaNiO₃/Ni-PVC in 1 M and 5 M KOH at 25°C

Concentration of KOH (mol·l ⁻¹)	Roughness factor ρ	Total surface charge, q_T (mC·cm ⁻²)	Outer surface charge, q_o (mC·cm ⁻²)	Inner surface charge, q_i (mC·cm ⁻²)	$\alpha = \frac{q_i}{q_T}$	Note
1	16 ^a	–	–	–	–	Fresh electrode
1	–	103 ^b	60	43	0.41	Cycled (110 min.) electrode
1	59	227	39	187	0.82	The same electrode after staying 63 h in air and cycled 80 min
5	33 ^a	–	–	–	–	Fresh electrode
5	–	241 ^c	100	141	0.60	The same electrode after 225 min cycling
5	86 ^c	588	56	532	0.91	The same electrode after staying 116 h in air and cycled 105 min

^a ρ was determined in the potential region of ± 50 mV from open circuit potential.

^b Cycled between 0 to 0.64 V at 0.05 V·s⁻¹.

^c Cycled between 0 to 0.55 V at 0.05 V·s⁻¹.

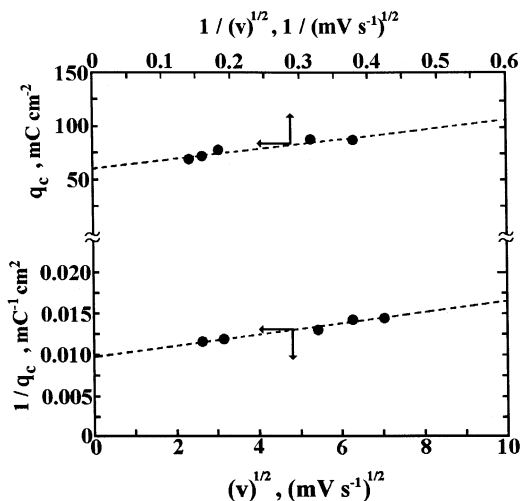


Fig. 9. Relationship plots between $1/q$ vs. $v^{1/2}$ and q vs. $1/v^{-1/2}$ for the $\text{LaNiO}_3/\text{Ni-PVC}$ electrode in 1 M KOH at 25°C.

repetitive potential cycling and exposure to air suggests, that the charge q_i refers to the whole thickness of the layer. It is necessary to consider that due to the porosity of the perovskite and non-uniformity of the perovskite layer on the Ni-PVC substrate, the electrolyte can penetrate and reach the substrate Ni-PVC. This is in agreement with the proportional increase of NiO as stated by XRD for the $\text{LaNiO}_3/\text{Ni-PVC}$ electrode after electrochemical aging. Besides that, it can explain the great increase observed in the total surface charge of the electrode after having been cycled and left in air. As ultimate evidence for the participation of the Ni-PVC in the LaNiO_3 behavior, there are visible lines (diffractogram c in Fig. 1), which correspond to $\text{La}(\text{OH})_3$.

3.4. Oxygen evolution reaction

The OER on pure lanthanum nickelate [5,9,10] and multiphase lanthanum nickelate [11–13] electrodes has been studied by several authors. Depending on the preparation method, the experimental conditions and the nature of supports employed in the preparation of LaNiO_3 , its physicochemical, interfacial electrochemical properties and the kinetic parameters for oxygen evolution/reduction might vary [9,14]. In our case it was encountered that the long-term anodic experiments showed a change in the composition and surface structure of the LaNiO_3 oxide.

Polarization curves obtained on stabilized $\text{LaNiO}_3/\text{Ni-PVC}$ electrodes in 1 and 5 M KOH solutions at room temperature are shown in Fig. 10. Two Tafel regions can be observed on these electrodes. However $\text{LaNiO}_3/\text{Ni-PVC}$ in 5 M KOH showed an approaching 'limiting current' from a low Tafel slope in the low overpotential region, to a high Tafel slope in the high

overpotential region. The 'limiting current' transition between Tafel regions on $\text{LaNiO}_3/\text{Ni-PVC}$ in 5 M KOH implies the existence of a parallel reaction or a mass transfer limited process. The break in the Tafel line could be attributed to the growth of the new oxide film and change in the surface structure of the perovskite oxide.

The alteration of composition and structure of the LaNiO_3 surface layers at high overpotentials, was demonstrated by XRD analysis (Fig. 1) of the sample $\text{LaNiO}_3/\text{Ni-PVC}$ preoxidized at 0.9 V in 5 M KOH (diffractogram c) and 1 M KOH (diffractogram b) over 19 h. The presence of $\text{La}(\text{OH})_3$ in the diffractograms suggests that very slight anodic dissolution of the $\text{LaNiO}_3/\text{Ni-PVC}$ electrodes occurs in the high overpotential region. Long-term experiments have been reported to manifest a time invariance of the electrode potential [5,9–11] but the possibility of anodic dissolution in the evolution of the service life has not been reported.

The line around $18^\circ 2\theta$ can be considered as a signal of a new phase (diffractogram c) formed from NiLa_2O_4 and LaNiO_3 when the Ni (II) in them is transformed into Ni (III) with the contribution of the Ni-PVC substrate. According to the X-ray diffraction pattern, it can be considered as a signal of a nickel hydroxide mixture. This consideration is supported by the X-ray diffractogram (where the same line was observed) obtained after drying the nickel hydroxide layers obtained on the Ni-PVC electrode by repetitive triangular sweeps between -1.0 and 0.6 V at 0.05 V s^{-1} sweep rate in 1 M KOH [21].

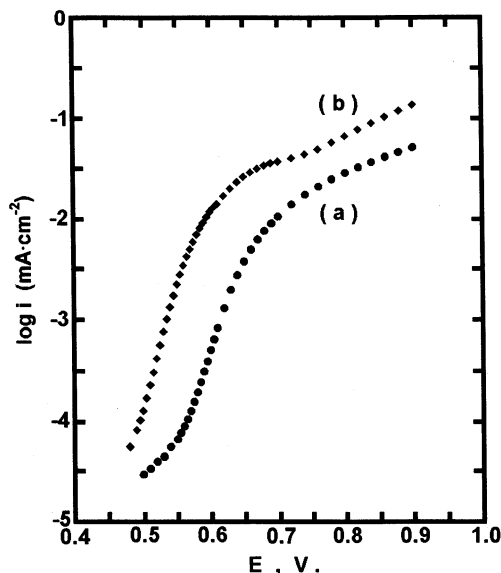


Fig. 10. Tafel plots (no iR correction was applied) for OER in 1 M KOH (a) and 5 M KOH (b) on the $\text{LaNiO}_3/\text{Ni-PVC}$ composite prepared via the propionic acid sol-gel process.

Table 3

Kinetic parameters for oxygen evolution on stabilized LaNiO₃/Ni–PVC electrodes

Concentration of KOH (mol·l ⁻¹)	q_c (mC·cm ⁻²)	b^a (mV·dec ⁻¹)	$\log i_0^b$ (mA·cm ⁻²)	i (700 mV) (mA·cm ⁻²)	i/q_c (mA·mC ⁻¹)	$\eta_{0.01}$ A·cm ⁻² (V)	$\eta_{0.1}$
1	67 ^c	48	-9.5	10.5	0.16	0.384	-
5	120 ^d	38	-9.1	37.0	0.31	0.291	0.417

^a At low overpotentials.^b Exchange current density in terms of apparent surface area.^c Cathodic charge involved during a potentiodynamic sweep run at 0.05 V·s⁻¹ between 0 and 0.64 V.^d Cathodic charge involved during a potentiodynamic sweep run at 0.05 V·s⁻¹ between 0 and 0.55 V.

Table 4

Kinetic parameters for oxygen evolution reaction on different LaNiO₃^a electrodes in 1 M KOH at 25°C

Electrode	b^b (mV·dec ⁻¹)	i_0^c (A·cm ⁻²)	i at $\eta = 0.3$ V (mA·cm ⁻²)	i at $\eta = 0.4$ V (mA·cm ⁻²)	Note
LaNiO ₃ /Ni–PVC	48	0.31×10^{-9}	5.2×10^{-1}	10.5	Synthesized via the propionic acid
LaNiO ₃ (pellet [18])	65	0.59×10^{-9}	0.25×10^{-1}	0.63	Synthesized by high-temperature solid-state reaction

^a X-ray analysis showed multi-phase lanthanum nickelate (LaNiO₃ + NiLa₂O₄ + NiO).^b At low overpotentials.^c Apparent exchange current densities.

Table 3 presents the corresponding kinetic parameters for the OER. One sees that the electrode activity is higher in 5 M KOH. A higher electrocatalytic activity in a more concentrated solution indicated by a lower Tafel slope (38 mV·dec⁻¹), the value of the oxygen overpotential at 0.01 A·cm⁻² and the apparent current density i or normalized to q_c (i/q_c) at 0.7 V can possibly be ascribed to the electrode surface. However, according to X-ray studies (Fig. 1) the alteration of the nature of the oxide film top layers also occurs, leading to changes in the microstructure of the film surface.

Values of the kinetic parameters for OER on the multiphase LaNiO₃ synthesized via the propionic acid and by high temperature solid-state reaction [13] in 1 M KOH are given in Table 4. This table shows that the multiphase LaNiO₃ synthesized via the propionic acid is more active as anode for the OER than the multiphase previously reported by Bockris-Otagawa [13].

We made some attempts to examine the catalytic activity of the LaNiO₃/Ni–PVC electrodes after prolonged potential cycling and OER measurements. The values of the kinetic parameters for 'aged' electrodes are summarized in Table 5. After prolonged potential cycling the activity of the LaNiO₃/Ni–PVC electrodes increased when the same electrodes were exposed to air for many days before being replaced in the cell. These results indicate that during potential cycling the number of active centers and the fraction of the non-activity surface have changed. The LaNiO₃/Ni–PVC in 1 M

KOH showed reproducible Tafel slopes, apparent current density and normalized current density suggesting good electrode stability. However, LaNiO₃/Ni–PVC showed a remarkably electrocatalytic activity in 5 M KOH after prolonged potential cycling and OER measurements. This may be related with the bulk characteristics of the substrate and with the surface composition. The last agrees with the different value of the Tafel slopes in 5 M KOH ($b = 38$ mV·dec⁻¹) and 1 M KOH ($b = 48$ mV·dec⁻¹).

4. Conclusions

X-ray analysis showed that when LaNiO₃ was synthesized via the propionic acid sol-gel route and calcinated in air at 850 or 900°C for 2.5 h in reality consisted of LaNiO₃, NiLa₂O₄ and NiO multi-phase. The layers of this oxide showed good adherence on the Ni–PVC substrate and interesting electrical properties. The characterization of these electrodes by cyclic voltammetry revealed that the effective utilization of the internal surface area of the LaNiO₃ layers can be increased by repetitive potential cycling as a result of changes in the inner and outer surface and participation of the Ni–PVC substrate. The proportion of LaNiO₃, NiLa₂O₄ and NiO compounds on the LaNiO₃/Ni–PVC electrode is altered after electrochemical treatment. On LaNiO₃/Ni–PVC electrodes during repetitive potential

Table 5
Stability of LaNiO₃/Ni-PVC electrodes as electrocatalysts for the oxygen evolution reaction at 25°C in KOH solutions

Concentration of KOH (mol·l ⁻¹)	q_c (mC·cm ⁻²)	b^a (mV·dec ⁻¹)	$\log i_0^b$ (mA·cm ⁻²)	i (700 mV) (mA·cm ⁻²)	i/q_c (mA·mC ⁻¹)	$\frac{\eta_{0.01}}{\eta_{0.1}}$ (V)		Note
						A·cm ⁻²	(V)	
1	67	48	-9.5	10.5	0.16	0.384	-	Cycled 110 min
1	87 ^c	46	-9.4	14.0	0.16	0.372	-	After 2.6 days
5	120	38	-9.1	37.0	0.31	0.290	0.551	Cycled 225 min
5	131 ^d	38	-9.5	79.0	0.60	0.291	0.417	After 4.6 days

^a At low overpotentials.

^b Exchange current density in terms of apparent surface area.

^c Calculated after 110 min cycled between 0 and 0.64 V at $v = 50 \text{ mV s}^{-1}$.

^d Calculated after 105 min cycled between 0 and 0.55 V at $v = 50 \text{ mV s}^{-1}$.

cycling and prolonged anodic polarization, where extensive gas evolution reaction occurred, the catalytic activity did not decrease and the aggregation of LaNiO_3 particles and their adhesion to the Ni–PVC substrate are sufficiently strong.

The electrocatalytic efficiency of the LaNiO_3/Ni –PVC composite in the oxygen evolution reaction in alkaline media increased after electrochemical aging. The LaNiO_3/Ni –PVC electrode showed good reproducibility and stability by repetitive use of the same electrode. After prolonged anodic polarization at 0.9 V in 5 M KOH the alteration of composition and structure of the surface LaNiO_3 layers occurs. The predominant phase after polarization was NiO due to substrate participation.

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