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Electrochemical reactions of $\text{La}(\text{Ni,Cr})\text{O}_3$ and $\text{La}(\text{Ni,Fe})\text{O}_3$ in acidic aqueous solutions

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Abstract Voltammetry of immobilised microcrystalline perovskites $\text{La}(\text{Ni,Cr})\text{O}_3$ and $\text{La}(\text{Ni,Fe})\text{O}_3$ revealed that these oxides yield three types of reactions in acidic aqueous solutions (0.1 M HClO_4): irreversible oxidative dissolution of Cr-rich oxides, irreversible reductive dissolution of Fe-rich oxides, and a quasi-reversible reaction most likely related to alteration of the valencies of Cr, Fe and/or Ni in the solid state. The samples of $\text{La}(\text{Cr}_{1-x}\text{Ni}_x)\text{O}_3$ with $x = 0.3$ and 0.5 especially showed limited cycling stability that is particularly surprising in the very strongly acidic solution.

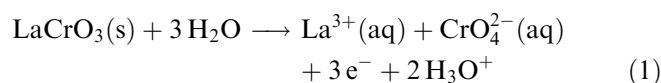
Key words Perovskite · Redox reactions · Iron oxides · Chromium oxides

Introduction

Electrochemical reactions of metal oxides are investigated for several reasons. Various oxides with the structure of perovskite, $(\text{M}_x^{\text{II}}\text{La}_{1-x}^{\text{III}})\text{MeO}_3$, where M^{II} is Ca, Sr or Ba, and Me is Fe, Co and/or Ni, have been proposed as electrocatalysts for oxygen evolution [1–4] and as conducting catalysts for fuel cells [5]. Recently, a series of electrochemical syntheses has been described for SrMeO_3 (perovskites) from $\text{SrMeO}_{2.5}$ (brownmillerite), where Me is Fe and/or Co [6–8]. In the mechanism of these reactions, the non-stoichiometry of the perovskites, particularly the vacancies in the oxide lattice, enabled by the variable valencies of the Me ions, play important roles. This kind of redox variability allows us to expect that the oxides could be dissolved at appropriate redox potentials and pH via a mechanism resembling reductive dissolution of ferric oxides and/or oxidative dissolution of chromic oxides [9, 10]. Never-

theless, dissolution reactions of perovskites such as LaMeO_3 , where Me is Cr, Fe and/or Ni, have not been systematically investigated.

We have recently described anodic dissolution of Cr-containing perovskites $\text{La}(\text{Cr,Ni})\text{O}_3$ and $\text{La}(\text{Cr,Fe})\text{O}_3$ [10] that proceeds according to the general equation:



This reaction is of the same nature as the chemical [9] and electrochemical [10, 11] oxidative dissolution of other Cr^{III} oxides. However, there is a possibility to substitute part of Cr in the crystal lattice by Ni, and the possible number of expected redox reactions is growing. For example, a question arises of whether it is possible to observe voltammetrically redox reactions of Cr^{III} and Cr^{IV} and/or Ni^{II} and Ni^{III} in the oxides. Note that this question is resembling that encountered in the voltammetric analysis of mixed-valence superconducting Cu oxides, which has been so intensively studied in the past decade [12–14].

Although reductive dissolution of many ferric oxide phases has been investigated, no attention has been paid to the perovskite LaFeO_3 . In this oxide, a part of the Fe constituents can also be replaced by Ni, and hence a similar question arises of what kind of electrochemical reactions can be observed employing voltammetric analysis of the resulting perovskites.

We synthesised several members of the perovskite series with the composition $\text{La}(\text{Fe,Ni})\text{O}_3$ and $\text{La}(\text{Cr,Ni})\text{O}_3$ and tested their electrochemical behaviour in an acidic aqueous environment. The simple and efficient technique of voltammetry of immobilised microparticles [15] (formerly referred to as abrasive stripping voltammetry) was employed. Beside the expected redox dissolution processes, we observed also a quasi-reversible reaction of these oxides in acidic solution. This reaction can be described as redox cycling of the metal ions in the perovskite lattice, accompanied by reductive decay in the case of the Fe^{III} perovskites.

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Experimental

Metal oxides were synthesised by a co-precipitation-heating procedure [16]. The boiling water solutions of appropriate amounts of $\text{La}(\text{NO}_3)_3$, CrCl_3 , $\text{Fe}(\text{NO}_3)_3$ and/or $\text{Ni}(\text{NO}_3)_2$ (each metal ion at a concentration ≤ 0.03 M) were precipitated by adding 15% excess of a 1 M solution of NaOH . The suspension was left to cool, the precipitate was filtered off and thoroughly washed with distilled water. The residue was left to dry under laboratory conditions and then heated at 1000°C in air for 1 h to 1 day until the phase composition of the perovskite was achieved. The single phase perovskites $\text{LaFe}_{0.25}\text{Ni}_{0.75}\text{O}_3$ and $\text{La}(\text{Ni},\text{Cr})\text{O}_3$ with a high content of Ni were prepared at the same temperature as reported in refs. [17] and [18], respectively. The phase purity was checked by X-ray diffraction (Siemens D5005, Germany).

Electrochemical measurements were performed with a potentiostat $\mu\text{Autolab}$ (Eco-Chemie, Utrecht, the Netherlands) in a three-electrode compartment with a saturated calomel electrode (SCE) reference electrode. The technique of voltammetry of immobilised microparticles has already been described in detail in our previous studies [10, 11, 19, 20]. The supporting electrolyte was 0.1 M HClO_4 with 0.4 M NaClO_4 ; it was deaerated by nitrogen.

Results and discussion

Two examples of cyclic voltammetric curves of the perovskites studied are given in Fig. 1. The partly reversible reaction is observed at around 0 V vs. SCE in

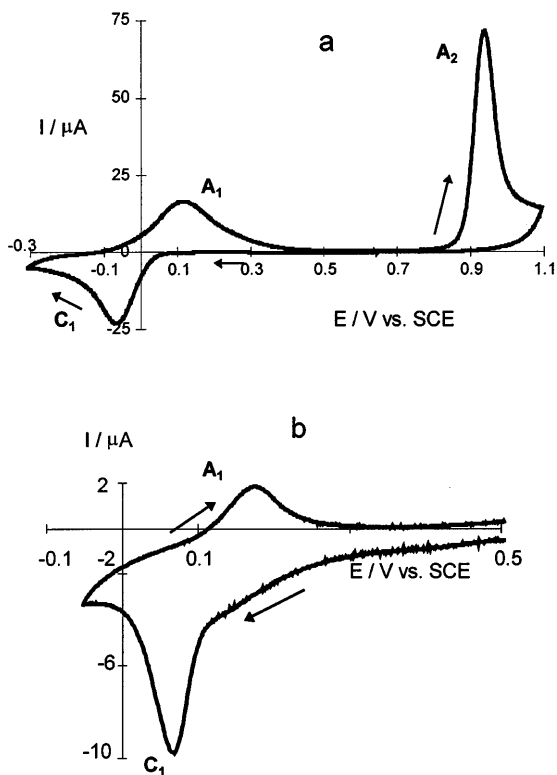


Fig. 1 a Cyclic voltammogram of $\text{La}(\text{Cr}_{0.5}\text{Ni}_{0.5})\text{O}_3$, the start at OCP at 0.3 V, the third scan in the range +0.3 to -0.3 V followed by anodic dissolution (A_2) (the first two scans between 0.3 and -0.3 V are omitted for clarity but shown in Fig. 2). b Cyclic voltammogram of $\text{La}(\text{Fe}_{0.7}\text{Ni}_{0.3})\text{O}_3$, start at OCP at 0.6 V, the first scan towards negative potentials. Scan rate 1 mV s^{-1}

the case of $\text{La}(\text{Cr},\text{Ni})\text{O}_3$ and $\text{La}(\text{Fe},\text{Ni})\text{O}_3$ (see the pair of peaks C_1/A_1 in Figs. 1–3). The overall reversibility of the C_1/A_1 process is demonstrated in Figs. 2 and 3. As is obvious, the stability of the cyclic voltammetric curves is much better in the case of $\text{La}(\text{Cr},\text{Ni})\text{O}_3$, and it is better when the Ni/Cr ratio is smaller (Fig. 2). The possible nature of this process will be discussed below. The voltammetric spectra of both perovskites also contain peaks caused by electrochemical dissolution.

At a potential above 0.8 V vs. SCE, $\text{La}(\text{Cr},\text{Ni})\text{O}_3$ is oxidatively dissolved (peak A_2 in Fig. 1a), as was experimentally proved using voltammetry with a carbon-paste electrode [10]. Because the only final products of the oxidative dissolution could be chromate (see Eq. 1) and Ni^{2+} (which is a stable soluble Ni species in acidic aqueous solution), the reaction responsible for the peak A_2 of $\text{La}(\text{Cr}_{0.5}\text{Ni}_{0.5})\text{O}_3$ can be written as:

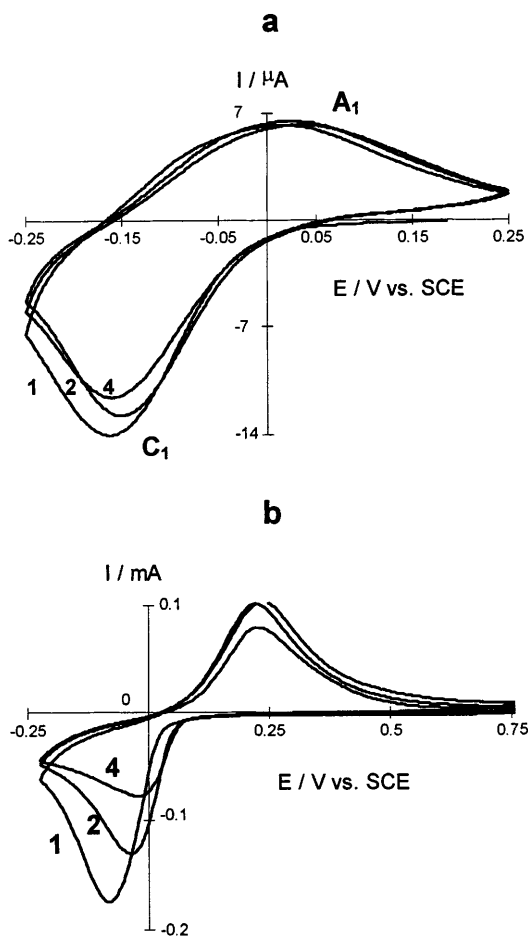
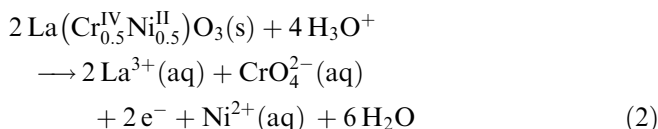


Fig. 2 a Cyclic voltammetry of the sample $\text{LaCr}_{0.7}\text{Ni}_{0.3}\text{O}_3$ between +0.25 and -0.25 V and b $\text{LaCr}_{0.33}\text{Ni}_{0.67}\text{O}_3$. The first, second and fourth scans are shown. Scan rate 1 mV s^{-1}

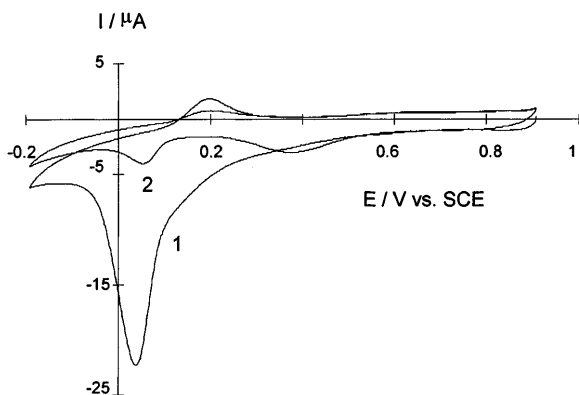
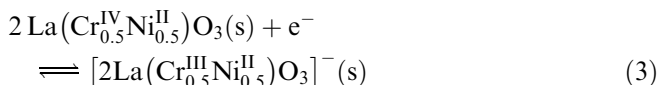


Fig. 3 Cyclic voltammetry of $\text{La}(\text{Fe}_{0.5}\text{Ni}_{0.5})\text{O}_3$. The first two scans between OCP at 0.9 V and -0.2 V at 1 mV s^{-1}

The valencies of the Cr and Ni ions in the lattice of the ternary perovskite were denoted as IV and II, respectively, according to the study of Zhang et al. [23]. It is obvious that even if the valencies of both Cr and Ni were III, or even if the perovskite samples were non-stoichiometric, for example, oxygen deficient, the oxidative dissolution should have proceeded according to an overall chemical reaction very similar to Eq. 2.

In contrast to peak A_2 , it is hard to identify the process responsible for the peaks C_1/A_1 (see Figs. 1–3), because such reactions of perovskite oxides in an acidic aqueous environment have not been described. The reaction can be similar to the electrochemical intercalation of Li^+ into $(\text{La},\text{Li})_{1-y}\text{TiO}_3$ and $\text{LiLaNb}_2\text{O}_7$ in a non-aqueous solution [21, 22]. It could be theoretically interpreted as some reversible reaction of metal ions in the oxide, e.g., $\text{Cr}^{\text{IV}}/\text{Cr}^{\text{III}}$, that could formally be written as:

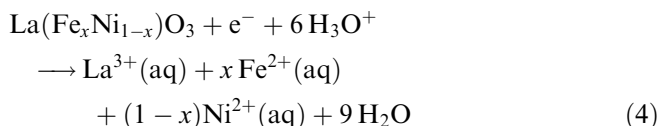


where square brackets denote a hypothetical solid reaction product that can arise only if the negative charge is compensated by the insertion of cations, such as H^+ or Na^+ , or by some other exchange of ions between the solid oxide and supporting electrolyte. The formal validity of this model could be supported by a comparison of the charges obtained by integration of peaks A_1/C_1 and that of A_2 with charges according to Eqs. 3 and 2,

respectively. The corresponding results obtained by voltammetry and chronoamperometry for $\text{La}(\text{Cr}_{0.5}\text{Ni}_{0.5})\text{O}_3$ are given in Table 1.

The results of the corresponding measurements and calculations for samples of $\text{La}(\text{Cr}_{0.7}\text{Ni}_{0.3})\text{O}_3$ and $\text{La}(\text{Cr}_{0.33}\text{Ni}_{0.67})\text{O}_3$ are summarised in Table 2. In the latest sample, the actual valencies of Cr and Ni in the perovskite are not clear. According to Zhang et al. [23], Cr^{V} could be expected, but the presence of Ni^{III} besides Ni^{II} cannot be excluded, and so it is hard to predict the extent of the quasi-reversible redox alteration of $\text{La}(\text{Cr}_{0.33}\text{Ni}_{0.67})\text{O}_3$ with respect to its oxidative dissolution. In all other cases the experimentally obtained ratios of the charges corresponding to quasi-reversible (cycling) and irreversible (dissolution) processes are rather close to the values based on Eqs. 3 and 2. The cycling stability of $\text{La}(\text{Ni},\text{Cr})\text{O}_3$ decreases with the growing amount of Ni. As far as we know, similar reversible cycling has been observed only in the case of $(\text{La},\text{Sr})(\text{Ni},\text{Co})\text{O}_3$ in alkaline solutions [2–4], but we observed the reaction to proceed in very strongly acidic solution. The cycling stability of $\text{La}(\text{Cr}_{1-x}\text{Ni}_x)\text{O}_3$ with $x = 0.3$ and 0.5 in 0.1 M HClO_4 is especially surprising. A $\text{La}(\text{Cr}_{0.85}\text{Ni}_{0.15})\text{O}_3$ sample was also investigated, but the cathodic process C_1 yielded only a flat voltammetric wave at 1 mV s^{-1} . $\text{La}(\text{Cr}_{0.95}\text{Ni}_{0.05})\text{O}_3$ was not electro-active except of its anodic dissolution.

In contrast to $\text{La}(\text{Cr},\text{Ni})\text{O}_3$, $\text{La}(\text{Fe},\text{Ni})\text{O}_3$ dissolves simultaneously with quasi-reversible redox cycling, as follows from the facts that A_1 is much smaller than C_1 (see Fig. 1b) and that the current decreases substantially in subsequent scans. The Fe-containing samples are probably reductively dissolved in a manner similar to that of the wide variety of ferric oxides [9–11], that proceeds actually at potentials close to 0 V vs. SCE in dilute mineral acids. In the case of the $\text{La}(\text{Fe},\text{Ni})$ perovskite, the reductive dissolution can be described by:



Because the reductive dissolution of ferric oxides proceeds just via the reduction of surface ferric ions to ferrous ones, any reversible reaction resembling that described by Eq. 3, but based either on $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}$ and/or $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$

Table 1 Charges (mC) corresponding to the processes C_1 , A_1 and A_2 corresponding to Fig. 1a, and obtained by voltammetry (VA) and chronoamperometry ($I-t$). Sample $\text{La}(\text{Cr}_{0.5}\text{Ni}_{0.5})\text{O}_3$. Calculated values based on Eqs. 2 and 3 are $Q_{C1}/Q_{A1} = 1$ and $Q_{C1}/(Q_{A1} + Q_{A2}) = 1/3$

Method	C_1	A_1	A_2	Charge ratios
VA (1 mV s^{-1})	3.0	3.9	4.9	$Q_{C1}/Q_{A1} = 0.77$ $Q_C/(Q_{A1} + Q_{A2}) = 0.44$
$I-t$ -0.02 V for 2500 s +0.02 V +0.15 V	3.6	1.4 1.9		$Q_{C1}/Q_{A1} = 1.1$ $Q_{C1}/(Q_{A1} + Q_{A2}) = 0.38$
$I-t$ +1.00 V up to dissolution -0.02 V for 1000 s +0.02 V for 500 s +0.15 V for 500 s +0.97 V up to dissolution	4.0	1.7 2.5	6.1 10	$Q_{C1}/Q_{A1} = 0.95$ $Q_C/(Q_{A1} + Q_{A2}) = 0.28$

Table 2 The ratios of charges corresponding to processes C_1 , A_1 and A_2 for the samples $\text{La}(\text{Cr}_{0.7}\text{Ni}_{0.3})\text{O}_3$ and $\text{La}(\text{Cr}_{0.33}\text{Ni}_{0.67})\text{O}_3$

Sample	Q_{C1}/Q_{A1}		$Q_C/(Q_{A1} + Q_{A2})$	
	Calculated	Experimental	Calculated	Experimental
$\text{La}(\text{Cr}_{0.7}\text{Ni}_{0.3})\text{O}_3$	1	1.1 ($I-t$) 0.83 (VA)	0.14	0.17 ($I-t$) 0.11 (VA)
$\text{La}(\text{Cr}_{0.33}\text{Ni}_{0.67})\text{O}_3$	1	0.70 (VA)	?	0.35 (VA)

cycling, should lead inevitably to the simultaneous decay of the solid phase according to Eq. 4. However, the potential of the pair of voltammetric peaks C_1/A_1 is in a potential region similar to that of $\text{La}(\text{Cr},\text{Ni})\text{O}_3$, that intimates a similar physicochemical nature of these reversible processes in Cr and Fe perovskites. While the reductive dissolution of non-substituted LaFeO_3 is slow under the given conditions (only an unclear voltammetric wave arises, not shown here), the more Ni that is present in the Fe perovskite, the more pronounced are both the voltammetric peaks C_1 and A_1 , but the faster is the decrease of the current in a subsequent voltammetric cycle.

The reaction corresponding to the voltammetric peaks C_1/A_1 could also be related to the deficiency in the oxide lattice. For example, it is well known that the perovskite LaMnO_3 can adopt an excess of oxygen according to the actual heating conditions, which causes the presence of vacancies in cation sublattices, but the perovskite structure is preserved [24]. The perovskite structure of $\text{LaCr}_{0.6}\text{Ni}_{0.4}^{\text{III}}\text{O}_3$ is also retained in its fully reduced form $\text{LaCr}_{0.6}\text{Ni}_{0.4}^{\text{II}}\text{O}_{2.8}$ [25]. Anionic vacancies are common for perovskites synthesised in air if they contain Fe^{IV} and Ni^{III} . These vacancies could serve as a pathway for the diffusion of the ions counterbalancing the redox cycling such as that expressed by Eq. 3. That reaction and the cycling of $\text{La}(\text{Fe},\text{Ni})\text{O}_3$ can be triggered only by the electrochemical reaction of a surface pair of $\text{Cr}^{\text{IV}}/\text{Cr}^{\text{III}}$, $\text{Fe}^{\text{VI}}/\text{Fe}^{\text{III}}$ or $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$, which have free access to the solution of a counterbalancing cation. This surface reaction can then be followed by a diffusion of M^+ or by some oxygen species towards the particle core.

To distinguish electrochemical surface reactions of particulate reactant, such as dissolution of ferric or chromic oxides, from reactions controlled by diffusion in the solid phase, such as topotactic reduction of $\gamma\text{-MnO}_2$ or EMD to MnOOH in an alkaline medium, we have recently proposed application of the potential pulses during chronoamperometric measurement [10, 19]. The principle of the method is shown in Fig. 4. During the chronoamperometric experiment, a 5–15 s pulse is applied, which is sufficiently large to cause a measurable increase of the current, but sufficiently small not to change the nature of the rate determining step (10 mV was found to be appropriate [10, 19]). Here, the first current samplings follow 1 s after the pulse edges. This time should be enough for charging the interfaces involved in the reaction. The method is based on the basic principles of the heterogeneous kinetics of solid reactants. Surface electrochemical reactions proceed on the interface of a constant composition and so the change of

the intensive variables causes just a change of the reaction rate but does not alter the reacting interface structure. The current response of a surface electrochemical reaction on the rectangle potential pulse (Fig. 4, curve 1) is hence also roughly rectangular, and the deviations can be significant just in the first samplings of the current after the pulse edges (see curve 2). The relative current response on the pulse can be expressed as the fraction

$$CR = \frac{I_{B+\Delta}}{I_B} \quad (5)$$

where $I_{B+\Delta}$ is the current during the potential pulse, and I_B is the current expected if the potential pulse was not applied. During one experiment, the value of CR is related to a formal charge transfer of the electrochemical reaction [10, 20], and CR does not depend on the reaction extent, because the structure of the 2-D reacting interface is constant during the reaction.

In contrast to the case of a surface reaction, if the reaction is controlled by a solid state diffusion step, the actual reaction rate depends on the actual concentration profiles of the reactants and/or products. The time necessary for establishing the concentration profile is comparable to the time necessary for almost total reaction. After each several seconds long potential pulse, the structure of the 3-D reacting interface should be disturbed and start to newly establish, following the Fick laws. These violations of equilibrium will cause typical fast changes of the current response (see curve 3 in Fig. 4). In principle, the current response resembles that

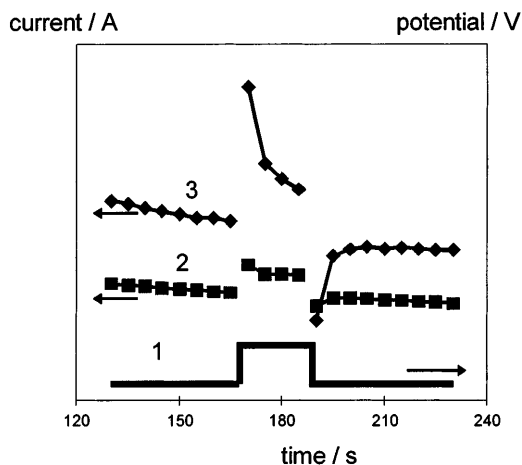


Fig. 4 The scheme of the current response of potential pulse chronoamperometry. Curve 1, potential programme; curve 2, the current response of surface reaction; curve 3, the current response of the diffusion controlled reaction (for more details see [10, 20])

of the double-potential step experiments used to study intercalation kinetics. In the present case of potential pulse chronoamperometry, the current responses should also depend on the reaction extent, because the structure of the reacting interface changes during the whole reaction as the diffusion continuously progresses towards the particle cores. Hence, one can conclude that if the reaction rate is controlled by solid state diffusion, not only the shape of the current response but also the actual value of CR must depend on the reaction extent. Note that the same rectangular shape and the same height of this rectangle is to be expected in the case of the surface reaction (see above). Unfortunately, it is obvious that it is hard to solve quantitatively the problem of the current response for the general case of a diffusion-controlled reaction of finite particles. Because the corresponding solution is not available and it would significantly exceed the frame of this report, we further utilise just the qualitative description of the current response for those two considered cases of heterogeneous kinetics.

A typical example of the current responses obtained by monitoring the cathodic process C_1 of $\text{La}(\text{Cr},\text{Ni})\text{O}_3$ using potential pulse chronoamperometry is shown in Fig. 5. The process seems to be controlled by a surface reaction on the 2-D interface in its early stage, but the contribution of a diffusion process in a 3-D zone grows at the later stage of the reaction, as is demonstrated by the distorted shape of the formerly rectangular current response. In that plot, Q denotes the actual charge of the remaining electrochemical process, Q_{TOT} is the total charge passed during the whole reaction, and I is the actual current [11, 20]. Note that not only the shape but also the relative height of the current responses change as the reactant is consumed. In Fig. 5 the CR values are approximately 1.3, 1.4 and 1.9 during the first, second and third applied pulses at 15%, 50%, and 75% reaction conversion, respectively.

The most likely explanation of the electrochemical experiments is that the observed partly reversible reaction proceeds according to Eq. 3, its initial rate is controlled by some kind of electrochemical equilibrium which is establishing on the surface of the perovskite

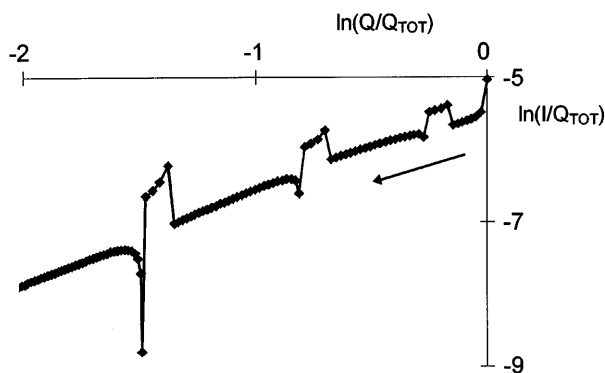


Fig. 5 The reaction curve based on the potential pulse chronoamperometry of $\text{LaCr}_{0.7}\text{Ni}_{0.3}\text{O}_3$, process C_1 , potential -0.03 V/SCE, three 10 mV pulses. The arrow indicates the reaction course

crystals, and its finishing is controlled by the solid state diffusion of the ions counterbalancing the redox alterations of the metal ions in the perovskite lattice.

Conclusion

The perovskites $\text{La}(\text{Cr},\text{Ni})\text{O}_3$ and $\text{La}(\text{Fe},\text{Ni})\text{O}_3$ exhibit a quasi-reversible electrochemical reaction in aqueous acidic solution, most likely related to the redox alteration of the valence of Cr, Fe and/or Ni ions in the perovskite lattice. In the case of $\text{La}(\text{Fe},\text{Ni})\text{O}_3$, this reaction is overlapped with reductive dissolution that causes a sharp decrease of the electrochemical activity during cyclic voltammetry. In contrast, the sample $\text{LaCr}_{0.5}\text{Ni}_{0.5}\text{O}_3$ yields relatively stable cyclic voltammetric curves at a potential range from -0.3 to $+0.3$ V vs. SCE in 0.1 M HClO_4 .

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