Samarium Additive Effect onto the Nickel Electrodeposition Process

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In the present work, nickel-samarium coatings (Ni-Sm) with 1.88% of samarium were obtained by electrodeposition from a nickel electrolyte composed of \( \text{H}_2\text{H}_2\text{SO}_3 \), \( \text{NiCO}_3 \), and \( \text{H}_2\text{BO}_3 \) and containing \( \text{Sm}_2(\text{SO}_4)_3 \). The electroactivity intervals of each component of the electrolytic bath and the effect of samarium (III) on the nickel electroplating process were studied by cyclic voltammetry and by electrochemical impedance spectroscopy (EIS). The results indicate that \( \text{H}_2\text{BO}_3 \) and \( \text{Sm}_2(\text{SO}_4)_3 \) added to the electrolytic bath are both reduced during the nickel electroplating. The Ni-Sm coatings were characterized using scanning electron microscopy (SEM), X-ray Diffraction (XRD), X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS). The results indicate that the samarium species incorporated in the nickel coatings are found as Sm(III) and Sm(II) hydroxides or oxides.

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Rare earth–transition metal alloys and nanocomposites have been attracting researcher’s interest because of their excellent magnetic, hydrogen absorbing and catalytic properties. The incorporation of rare earth compounds into the coatings, especially of cerium oxide (CeO₂) into a nickel coating, has been shown to improve the wear, corrosion and oxidation resistance, as well as the hardness and catalytic properties.1–7 Electrodeposited Ni/CoCe₂ nano-composite coating showed improved microhardness, corrosion resistance and wear resistance when compared to Ni.4

Samarium is another rare-earth element that, in close analogy with the behavior of cerium, also forms thin films capable of protecting the metallic substrates from corrosion attack.8 Recently, Nickel coatings obtained by electrodeposition, from a sulfamate bath in the presence of Samarium (III), showed improved corrosion resistance.9

Usually, the incorporation of rare earth compounds into the coatings are obtained using an electrolytic bath, which contains rare earth nanoparticles or microparticles suspended in the electrolyte; these particles are embedded in the electroplated layer by applying an electrical current. Nevertheless, the possibility of obtaining a homogenous co-deposit of these particles in the matrix of Ni is very complicated and depends on many factors, such as particle size and distribution uniformity in the electrolyte.

A new procedure for the creation of a Ni-CeO₂ composite coating was studied through the simultaneous electrodeposition of the metal and cerium oxide without the addition of CeO₂ particles in the electrolytic bath.10 Likewise, this procedure can be used for the incorporation of samarium compounds on Ni coatings.9

Although studies have been reported on the deposition of rare earth and rare earth alloys produced by electroplating, the mechanism is not clear yet.8,10–12 The aim of this work was to study the role of the samarium (III) during the Ni electroplating on a Pt substrate from a sulfamate electrolyte. Electrochemical studies were carried out by cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

Experimental

The studies of nickel electrodeposition were performed using an electrolytic bath containing \( \text{NH}_2\text{H}_2\text{SO}_3 \), \( \text{NiCO}_3 \), \( \text{H}_2\text{BO}_3 \) with and without the addition of \( \text{Sm}_2(\text{SO}_4)_3 \). A potentiostat/galvanostat Autolab PGSTAT30 and a conventional three electrode electrochemical cell were used to apply the electrochemical techniques. A platinum working electrode (BAS brand) with an area of 0.02 cm² (WE), a platinum auxiliary electrode (AE), as well as a saturated calomel reference electrode (RE) were used during the process. Before each experiment, the dissolutions were deoxygenated by bubbling ultra-pure nitrogen (Praxair) for 30 minutes, and an N₂ atmosphere along with a 25°C controlled temperature was maintained during the experiments.

The cyclic voltammetry experiments were performed initiating with a cathodic sweep from the potential corresponding to open-circuit potential, applying different potential inversions and finalizing at the equilibrium potential. Most of the experiments were performed using a scan rate of 50 mV/s.

The tests of electrochemical impedance (EIS) were conducted at a frequency range of 100 kHz to 10 mHz, at an amplitude of 10 mV AC. Before each EIS experiment, a potential pulse was applied (the corresponding potential to each EIS experiment) during a 200 s time lapse, with the aim to stabilize the system before the impedance experiments were carried out. The nickel electroplatings were realized by applying a pulse potential of −1.2 V vs. SCE (over a time of 180 s) on a steel substrate submerged in an electrolytic bath consisting of \( \text{NH}_2\text{H}_2\text{SO}_3 \), \( \text{NiCO}_3 \), \( \text{H}_2\text{BO}_3 \) with and without the addition of \( \text{Sm}_2(\text{SO}_4)_3 \). The obtained coatings were characterized using scanning electron microscopy (SEM), X-ray Diffraction (XRD), X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS). The spot size for the XPS measurements was 400 mm.

Results and Discussion

Study of the components in the electrolytic bath.—With the intent to identify the electroactivity intervals of each of the components of the electrolytic bath, a cyclical voltammery study was first performed on the supporting electrolyte (dissolution of 0.58 M \( \text{NH}_2\text{H}_2\text{SO}_3 \), at a \( \text{pH} = 3 \)). The obtained results are shown in Fig. 1.

In these cyclic voltammograms, it can be seen that during the cathodic sweep two reduction processes take place, and their respective oxidation processes occur during the anodic sweep. The beginning of the first reduction process is observed at a potential of −0.396 V vs. SCE and corresponds to the reduction/sorption stage of \( \text{H}^+ \) on the platinum surface.3,13,14 The process of hydrogen evolution can be observed at a more negative potential (less than −0.90 V vs. SCE). This indicates that only two main reactions take place in this solution, involving the reduction/sorption steps of \( \text{H}^+ \) and the release process.

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of H₂. It is clear that there are not other electroactive species in the potential range studied.

Once the electroactivity limits of the supporting electrolyte were studied, cyclic voltammetry with potential inversions were performed using a dissolution of sulfamic acid with boric acid, composed of the following: 0.58 M of NH₂HSO₃ and 0.32 M of H₃BO₃, at pH = 3. The results indicate that in addition to the reduction processes H⁺/H ads (at −0.396 V vs. SCE) and the generation of H₂ (at −0.90 V vs. SCE), noted previously, a reduction process occurs due to the presence of H₃BO₃ (Fig. 2). This process occurs in a potential range of −0.586 V vs. SCE and may correspond to the reduction of boric acid to diborane as shown in Reaction 1.15

\[
2\text{H}_3\text{BO}_3 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \tag{1}
\]

The effect of boric acid during the electrodeposition of Ni has been previously studied.16 The results indicate that boric acid prevents the formation of Ni(OH)₂ on the electrode surface and favors the formation of a more compact and less faulty Ni plating. This may be possible because the reduction reaction of boric acid competes with hydrogen reduction reaction and this, in turn, reduces the hydrogen evolution reaction,15 which causes an increase in the pH interphase and the formation of Ni(OH)₂.

To study the electroactive behavior of samarium, dissolution with the following composition was used: 0.58 M of NH₂HSO₃ and 8.2 mM of Sm³⁺, at pH = 3. The results obtained are shown in Fig. 3. In these voltammograms, the reduction process of the Sm³⁺ can be observed (≈−0.80 V vs. SCE). In an anodic sweep, the process corresponding to oxidation in a potential range of −0.60 V vs. −0.55 V vs. SCE can be observed.

To confirm the reduction process of Sm³⁺, a study by cyclic voltammetry was conducted varying the concentration of samarium (2.7 mM Sm³⁺ to 8.2 mM Sm³⁺) in a base solution of NH₂HSO₃ 0.58 M. Cyclic voltammetry have been carried out in a potential range of −0.9 V to 0.5 V to prevent hydrogen evolution reaction. These results demonstrate the presence of a reduction process in a potential of ≈−0.8 V vs. SCE (Fig. 4), and its corresponding oxidation process in a potential of ≈−0.55 V vs. SCE. The intensity of these peaks increases considerably with the concentration of Sm³⁺ in the solution. It is evident that these...
The overlapping phenomenon sweep, an overlap appeared. This reduction process may correspond to the reduction of H3BO3, C) the third at a potential of 0.1 M NaCl solution.17 Of samarium (III) on platinum was observed by H. Ilkhani et al. in a reduction process of Sm3+

Effect of samarium (III) on the nickel electroplating process.—Fig. 8 shows the cyclic voltammograms obtained from a solution of Ni sulfamate with and without the addition of samarium. Cyclic voltammetry of Ni reduction process from a solution without samarium. Cyclic voltammetry obtained in a dissolution of sulfamic acid and boric acid (Fig. 2); indicating that the presence of boric acid in the dissolution favors the formation of this film. To verify the formation of this film, a potential pulse of −1.2 V vs. SCE was applied on a steel electrode for 180 s. Figs. 7a and 7b show the SEM image of the substrate surface, before and after applying the potential pulse. These results indicate that effectively, under these conditions, a film on the substrate is formed; an X-ray fluorescence analysis allowed the verification of the samarium presence.

The formation mechanism of this samarium film is similar to the process of cerium film formation.19 It can be explained by the process described by E. J. Ruiz et al.,12 which related the formation of a hydroxide film generated by the local increase of pH on the electrode surface, as indicated by the following reactions:

\[2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \[Sm^{3+} + 3OH^- \rightarrow Sm(OH)_3 \]  \[Sm(OH)_3 \rightarrow Sm_2O_3 + 3H_2O \]  \[Sm^{3+} + e^- \rightarrow Sm^{2+} \]  \[2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \[Sm^{3+} + 2OH^- \rightarrow Sm(OH)_2 \]

In Fig. 6, the voltammograms obtained in a dissolution containing the three bath components, 0.58 M of NH2HSO3, 0.32 M of H3BO3 and 2.7 mM of Sm3+ at a pH = 3 are shown. The results indicate the presence of three reduction processes before the hydrogen evolution: A) the first at a potential of −0.396 V vs. SCE corresponding to the reduction H+/Hads, B) the second at a potential of −0.586 V vs. SCE corresponding to the reduction of H3BO3, C) the third at a potential of −0.90 V vs. SCE (Epc) and corresponds to the reduction process of samarium. These results verify that all processes observed in these voltammetries correspond with the results obtained in the individual study of each of the bath components.

In addition to the above described processes, a reduction process at a potential of −1.0 V vs. SCE can be observed. Also, during the anodic sweep, an overlap appeared. This reduction process may correspond to the reduction of Sm2++/Sm3+. The reduction of samarium (III) on platinum was observed by H. Ilkhani et al. in a 0.1 M NaCl solution.17 To complement this study, cyclic voltammograms were performed at different scan rates (Fig. 5a) to obtain the ratio of jpc vs. ν1/2 proposed by the Randles-Sevick equation.18 The observed behavior is linear with the ordinate equal to zero. The adjustment was made using the OriginPro 8 software (Fig. 5b). According to these results, the reduction process of Sm3+/Sm2+ is controlled by diffusion.

In the study of samarium, in the absence of boric acid (Fig. 3), or in the presence of three reduction processes: A) the first at a potential of 0.90 V vs. SCE (Epc) and corresponds to the reduction process of cerium film formation.19 It can be explained by the process described by E. J. Ruiz et al.,12 which related the formation of a hydroxide film generated by the local increase of pH on the electrode surface, as indicated by the following reactions:

\[2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \[Sm^{3+} + 3OH^- \rightarrow Sm(OH)_3 \]  \[Sm(OH)_3 \rightarrow Sm_2O_3 + 3H_2O \]  \[Sm^{3+} + e^- \rightarrow Sm^{2+} \]  \[2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \[Sm^{3+} + 2OH^- \rightarrow Sm(OH)_2 \]
and corresponds to the reduction of H⁺ on the platinum surface. At a more negative potential (−0.54 V vs. SCE), the beginning of a second cathodic process can be discerned. This process may be due to an adsorption process and/or reduction of H₂BO₃. Minami et al. found a cathodic process in this same potential region, which they attributed to a reduction process of boric acid. This reduction process, a third cathodic process can be discerned, which starts at a potential of −0.9 V vs. SCE. This process corresponds to the reduction of Ni²⁺ along with the hydrogen evolution reaction. Finally, in the anodic sweep, the anodic process A1 can be seen, which corresponds to the oxidation of Ni.

Unlike the behavior described above, cyclic voltammetry obtained with the presence of samarium presents four reduction processes (C1, C4, C5, C6). It indicates that during electroplating of Ni from a dissolution containing samarium, there will be at least one additional process (samarium reduction). The cathodic process C1 is not significantly affected by the addition of samarium in the dissolution. The cathodic process C4 occurs in the same potential region as the C2 process, observed in the absence of samarium, only with a slightly larger current intensity; thus it is attributed to an adsorption and/or reduction process of H₂BO₃ affected by the presence of samarium in the dissolution. In a negative potential region of (−0.85 V vs. SCE to −1.0), the C5 cathodic process takes place, which can be attributed to adsorption and/or reduction of samarium on the electrode surface. The reduction process of Sm³⁺ to Sm²⁺ was previously observed during the study of the components of the electrolytic bath (Fig. 6). Finally, the C6 reduction process should be related to the electroplating of Ni accompanied by the hydrogen evolution reaction. In this case, it takes place at a potential of −1.0 V vs. SCE. This potential is about 100 mV more negative than the potential at which this process occurs in the absence of samarium (C3). It is possible that due to the formation of a samarium film on the electrode surface, an overpotential was generated for the reduction of nickel (as shown in Fig. 8). Apparently, the process of reducing Ni was considerably altered by the presence of samarium in the dissolution. This may be due to a competition between the reduction reaction of Ni and the reduction reaction of samarium or the film formation on the substrate.

Electrochemical impedance study.—The potential region selected for this study was −0.8 to 1.0 V vs. SCE because in this range the reduction process of Ni and the adsorption/reduction process of samarium take place. Fig. 9 shows Nyquist diagrams which were obtained from Ni sulfamate dissolution in the absence of samarium. These results indicate that all spectra obtained show two loops, a first capacitive loop at high frequencies and a second loop of lower frequencies domain. The first loop is related to the double layer charge transfer, while the second loop is linked to the process of reducing hydrogen or Ni, depending on the applied potential. So that, the spectrum obtained at a potential of −0.8 V vs. SCE (Fig. 9a) defines the formation of a second capacitive domain loop in the low-frequency range (less than 1 Hz). This can be associated with adsorption and/or reduction of H⁺ which prevails in this potential range. When the potential becomes more negative (−0.85 to −0.9 V vs. SCE), the second capacitive loop disappears (which is shown at frequencies below 1 Hz) and the formation of an inductive loop occurs. In this potential region, the adsorption and/or reduction stages of Ni become relevant in the process. A similar behavior was observed by A. P. Ordine et al. during a study by electrochemical impedance using a solution of NiSO₄.

The presence of an inductive loop at frequencies lower than 1 Hz was also observed by Epelboin et al. in a Watts-type bath; and is attributed to adsorption of the monovalent species (NiOH)ads, which plays an important role as an intermediate species in the electroplating mechanism of Ni. It indicates that the electroplating mechanism of Ni from a sulfamate bath can be similar to that of a Watts-type bath mechanism.

In Fig. 10, the impedance spectra obtained in the presence of samarium are displayed. The behavior is very like the behavior obtained in its absence. The main difference is related to the diameter of the first semicircle (associated with charge transfer resistance), all spectra show greater charge transfer resistance, regarding the spectra obtained at a same potential in the absence samarium.
Figure 9. Impedance spectra obtained from a dissolution with 0.58 M of NH₂HSO₃, 0.57 M of Ni(CO₃)₂, and 0.32 M of H₃BO₃ at pH = 3, applying a potential of: a) −0.8 V, b) −0.85 V, c) −0.90 V, d) −1.0 V.

Table I summarizes the resistance values of the dissolution (Rₛ), and the charge transfer resistance of (Rₓ) obtained using the equivalent circuits shown in Fig. 11. The obtained results confirm that the charge transfer resistance is significantly higher in the presence of a 24.6 mM of Sm³⁺ in solution. This increase in charge transfer may be due to the formation of a samarium hydroxide film on the electrode surface.

Characterization of coatings.—The morphology of Ni coatings in the presence and absence of samarium are presented in Fig. 12. In these images, the coating without samarium shown a characteristically nodular morphology for nickel electroplating obtained from an electrolytic bath without additives. Instead, the Ni plating with 1.88% of samarium (composition determined by X-ray fluorescence), is modified considerably since the image of this coating shows the presence of micro-fissures in the coating. It is an indication that there was an increase in the internal stress generated by the incorporation of the samarium in the coating. A similar effect was observed in the elaboration of a nickel film with nanoparticles of CeO₂.

| Potential (V vs. SCE) | [Sm³⁺] = 0.0 Mm | [Sm³⁺] = 24.6 Mm |
|-----------------------|-----------------|------------------|
|                       | Rₛ, Ω.cm²       | Rₓ, Ω.cm²        | Rₛ, Ω.cm²       | Rₓ, Ω.cm²       |
| −0.80                 | 1.3             | 440.4            | 1.4             | 731.3            |
| −0.85                 | 1.4             | 38.6             | 1.3             | 84.7             |
| −0.90                 | 1.2             | 7.1              | 1.7             | 24.3             |
| −1.0                  | 1.2             | 2.2              | 1.7             | 53.5             |

XRD Study.—In Fig. 13, the spectra of X-ray diffraction for Ni coatings without and with samarium are shown. The electroplating of Ni shows a face-centered cubic crystal structure, with the preferential growth of (200) plane followed by the (111) plane, characteristic of Ni coatings obtained using an electrolytic bath of sulfamates. The Ni plating with 1.88% samarium has a crystalline structure with a preferential growth of (111) plane followed by the plane (220). It is evident that the co-deposition of samarium in the Ni plating modifies texture, a preferential orientation (200) changes to an (111). It is important to indicate that XRD does not allow demonstrating the presence of a kind of samarium compound in the coating, similar results were observed by H. Hasannejad et al. for CeO₂ coatings.

Fig. 14a displays the XPS spectrum of a Ni-Sm (1.88%) film on steel. This spectrum comprises the main lines of the elements present in the metallic nickel film and the substrate. The position of the carbon C1s line (284.15 eV), which was used as a reference, is typical of the lines from hydrocarbon compounds. Fig. 14b shown the XPS spectrum of Ni 2p level in electrodeposited Ni-Sm (1.88%) film, in which the Ni 2p indices and Ni 2p³/² peaks were found at peaks (852.38 and 869.68 eV) respectively. The peak at 852.38 eV is assigned to metallic nickel and the peak showed at 855.88 eV can be attributed to the NiO phase.
Figure 10. Impedance spectra obtained in a dissolution with 0.58 M of NH$_2$HSO$_3$, 0.57 M of Ni (CO$_3$)$_2$, 0.32 M of H$_3$BO$_3$ and 24.6 mM of Sm$^{3+}$, at pH = 3, and a potential of: a) $-0.8$ V, b) $-0.85$ V, c) $-0.90$, d) $-1.0$ V.

The XPS spectrum of Sm 3d consists of two components related to Sm(III) and Sm(II) (Fig. 14c). The two prominent peaks at 1083.18 eV and 1110.38 eV correspond to Sm(III)\cite{27,28}, whereas the weak peak pair at about 1090 and 1119 eV is ascribed to Sm(II)\cite{29}. The presence of Sm(II) in the coating coincides with the formation mechanism of the samarium film previously proposed, in which includes the reduction of

![Figure 11](image1.png)  
**Figure 11.** Equivalent circuits used for simulation of the impedance spectra.

![Figure 12](image2.png)  
**Figure 12.** Surface SEM image for Ni electrodeposits (10000X) with the following samarium concentration: a) 0% samarium, b) 1.88%.
Sm(III) to Sm(II). As shown in Fig. 14d, the O 1s core-level spectrum is characterized by the main peak at 531.18 eV, assigned to the oxygen of Sm(III)-O groups,\textsuperscript{27} this indicates that the Sm(III) in the film could be in the form of oxides (Sm$_2$O$_3$).

Conclusions

The results indicate that it is possible to obtain Ni coatings with samarium using an electrolytic bath containing NH$_2$HSO$_3$, Ni(CO$_3$)$_2$, H$_3$BO$_3$ and Sm$_2$(SO$_4$)$_3$. When the bath has a composition with a molar ratio of Ni(II)/Sm(III) equal to 69.27, a Ni coating of 1.88% of samarium can be obtained.

The analysis by XPS indicates that the samarium incorporated in the nickel deposits is found as Sm(III) species and the presence of Sm(II), which was demonstrated in the cyclic voltammetry the possibility of formation of a Sm(II) species during the electroplating of Ni.

The mechanism of incorporation of samarium in the nickel coating may be similar to that previously reported for the formation of cerium and samarium films. It is based on the generation of hydroxide ions (OH$^-$), at the interface metal-solution, as a result of the reduction of a soluble precursor on the substrate. According to this mechanism in a first stage, rare earth compounds are incorporated into hydroxides and subsequently can be converted into oxides.

References

1. J. Wang, R. Xu, and Y. Zhang, J. Rare Earth, 30(1), 43 (2012).
2. Y.-J Xue, X.-Z Jia, Y.-W Zhou, W. Ma, and J.-S Li, Surf. Coat. Tech., 200(20–21), 5677 (2006).
3. B. Han and X. Lu, Surf. Coat. Tech., 202(14), 3251 (2008).
4. S. T. Aruna, C. N. Bindu, V. Ezhil Selvi, V. K. William Grips, and K. S. Rajam, Surf. Coat. Tech., 200(24), 6871 (2006).

Figure 13. X-ray diffraction spectrum of Ni coatings (a) and Ni-Sm (b).

Figure 14. XPS spectrum of an electrodeposited Ni-Sm (1.88%) film on steel.
5. X. Peng, T. Li, and W. Wu, *Oxid. Met.*, 51(3), 291 (1999).
6. Z. Guo and X. Zhu, *Mat. Sci. Eng. A*, 363(1–2), 325 (2003).
7. N. M. Deraz, *J. Anal. Appl. Pyrol.*, 95, 56 (2012).
8. E. J. Ruiz, R. Ortega-Borges, L. A. Godínez, T. W. Chapman, and Y. Meas-Vong, *Electrochim. Acta*, 52(3), 914 (2006).
9. J. R. López, G. Stremmelsoerfer, G. Trejo, R. Ortega, J. J. Pérez, and Y. Meas, *Int. J. Electrochem. Sci.*, 7, 12244 (2012).
10. H. Hasannejad, T. Shahrabi, M. Jafarian, and A. SabourRoughgheat, *J. Alloy Compd.*, 509(5), 1924 (2011).
11. S. B. Jundale and C. D. Lokhande, *Mater. Chem. Phys.*, 38(4), 325 (1994).
12. V. Lair, L. S. Živković, O. Lupan, and A. Ringuedé, *Electrochim. Acta*, 56(12), 4638 (2011).
13. Y. P. Lin and J. R. Selman, *J. Electrochem. Soc.*, 140(5), 1299 (1993).
14. K.-D. Song, K. B. Kim, S. H. Han, and H. K. Lee, *Electrochem. Commun.*, 5(6), 460 (2003).
15. T. Mimani, S. M. Mayanna, and N. Munichandraiah, *J. Appl. Electrochem.*, 23(4), 339 (1993).
16. C. E. Dávalos, J. R. López, H. Ruiz, A. Méndez, R. Antaño-López, and G. Trejo, *Int. J. Electrochem. Sci.*, 8, 9785 (2013).
17. H. Ilkhani, M. R. Ganjali, M. Arvand, and P. Norouzi, *Int. J. Electrochem. Sci.*, 5, 168 (2010).
18. N. Aristov and A. Habekost, *World Journal of Chemical Education*, 3(5), 115 (2015).
19. S. Bohm, R. Greef, H. N. McMurray, S. M. Powell, and D. A. Worsley, *J. Electroanal. Chem.*, 147, 3286 (2000).
20. A. P. Ordine, S. L. Díaz, I. C. P. Margarit, O. E. Barcia, and O. R. Mattos, *Electrochim. Acta*, 51(8–9), 1480 (2006).
21. I. Epelboin, M. Joussellin, and R. Wiart, *J. Electroanal. Chem.*, 119, 62 (1981).
22. A. Godon, J. Creus, X. Feaugas, E. Conforto, L. Pichon, C. Armand, and C. Savalla, *Mater. Charact.*, 62, 164 (2011).
23. H. Zhao, L. Liu, J. Zhu, Y. Tang, and W. Hu, *Mater. Lett.*, 61(7), 1605 (2007).
24. E. Pompei, L. Magagnin, N. Lecis, and P. L. Cavallotti, *Electrochim. Acta*, 54(9), 2571 (2009).
25. É. P. Domashevskaya, S. V. Ryabtsev, V. A. Terekhov, A. S. Len’shin, F. M. Chernyshov, A. T. Kazakov, and A. V. Sidashov, *J. Struct. Chem.*, 52, Supplement, S115 (2011).
26. T. Toﬁnski, G. Chelkowska, B. Andrzejewski, A. Kowalczyk, M. Timko, and J. Kováč, *phys. status solidi a*, 196, 1, 294 (2003).
27. T.-D Nguyen, D. Mirabet, and T.-D On Do, *J. Phys. Chem. C*, 112(39), 15226 (2008).
28. M. Mo, K. S. Hui, X. Hong, J. Guo, Ch. Ye, A. Li, N. Hu, Z. Huang, J. Jiang, J. Liang, and H. Chen, *Appl. Surf. Sci.*, 290, 412 (2014).
29. F. Falsafi, B. Hashemi, A. Miraee, E. Fazio, F. Neri, N. Donato, S. G. Leonardi, and G. Neri, *Ceramics International*, 43, 1029 (2017).