Electrochemical study of the $LaNiO_3$ perovskite-type oxide used as anode in nickel-metal hydride batteries

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Abstract— The current work examines the hydrogen storage properties of LaNiO3, a perovskite-type oxide commonly used as a negative electrode in nickel-metal-hydride batteries. In the performed experiments, the LaNiO3 sample was synthesized employing the sol-gel method and its structure and electrochemical characteristics were systematically investigated. Through X-ray diffraction analysis, it was proven that the $LaNiO_3$ material consists of a single phase and crystallizes in the Pm-3m cubic space group. To assess the electrochemical performance of LaNiO, electrochemical measurements were carried out at 298K utilizing chronopotentiometry, cyclic voltammetry and electrochemical impedance spectroscopy with an electrolyte concentration equal to 6 Mole. As demonstrated by the obtained results, the $LaNiO_3$ electrode required only two cycles to be activated. In fact, it reached its maximum discharge capacity equal to 119 mAh. $g^{-1}$with a current density of 14.54 mA. g^{-1}. The exchange current density and the Nernst potential were studied by cyclic voltammetry. All electrochemical cycling tests showed that the electrode was activated in the 2ndcycle. It was also noticed that the values of the parameters obtained by the characterization methods evolved in the same way. Moreover, the charge transfer resistance and adsorption resistance were determined using the impedance technique. Overall, this study provides valuable information on the hydrogen storage behaviour of the $LaNiO_3$ alloy. These data may be useful for the development of hydrogen storage batteries.

Keywords –perovskite, $LaNiO_3$ type oxide; Nickel-metal hydride accumulators.

1. INTRODUCTION

In recent years, the increasing demand for new battery technologies, more precisely hydrogen storage batteries and Nickel-metal hydride battery that have long lifetime and high storage capacity, has generated a surge of interest in exploring novel materials for their development[1-4]. In the last two centuries, the sales of batteries have almost doubled, mainly due to the widespread of new mobile technologies such as cell phones, tablets and laptops. Moreover, the growing number of the electric and hybrid vehicles has led to the rise in the demand for advanced batteries with improved storage capacity. As a result, significant effort has been made to create new materials for Ni-MH battery technology that can be efficiently used in various operating conditions[5-8]. In fact, the Ni-MH battery [9-14]is intensively employed in several domains such as photoelectricity and electronics[15, 16], the medical field as well as the production of solar cells and hybrid or fully-electric vehicles. However, this new technology can be further explored and improved by optimizing the negative electrode through the introduction of new and less expensive materials having high hydrogen storage capacity as well as quick and sustainable charging/ discharging processes and considerable stability during the electro-chemical cycling[17-23]. Recent studies have explored the use of ABO_3perovskite-type oxides(first discovered by Esaka et al.) [24], where A is a large cation and B denotes a small transition metal cation. These perovskites exhibit excellent hydrogen absorption properties [25-36]. In fact, they are the most commonly-used mixed crystalline oxides defined as homogeneous solid phases containing several types of metal cations existing in different oxidation states.

Their electrochemical performance was evaluated in numerous research works, notably the studies conducted by G. Deng et al.[37, 38], who employed a stearic acid combustion method to prepare a $LaFeO_3$ alloy that provided a discharge capacity of 80 mAh. g^{-1}at 298K. The authors also used the same technique to prepare the LaCrO3 alloy which exhibited an electrochemical discharge capacity equal to194.8 mAh.g^{-1}

Moreover, Bhardwaj et al. [10] developed the $Sm_{1-x}Sr_xCoO_{3-\delta}$ (x = 0, 0.5, 1) perovskites and compared their discharging capacities. They concluded that the $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$oxidehad a maximum capacity of 182 mAh.g^{-1}at 298 K.

The authors also used the same method to prepare the $LaCrO_3$ alloy with an electrochemical discharge capacity equal to194 $mAh.g^{-1}$. Q. Wang fabricated the $LaFeO_3$ alloy [39] utilizing a similar method that achieved an electrochemical discharge capacity of 143.3 at 298K. The perovskite-type oxide $LaNiO_3$ is an innovative material employed in various applications, such as electrocatalysis[40], superconductivity [41], rechargeable zinc-air batteries [42], lithium-oxygen batteries [43]andLi-O_2 batteries [44],and as active material utilized in Ni-MH accumulators due to its easy synthesis and good electrochemical behavior at different temperatures. However, previous studies showed that perovskites have low electrochemical discharge capacity at 298K[45-47]. This problem is analyzed and solved in the present work.

In the performed experiments, Perovskite-type oxide $LaNiO_3$ alloy was utilized as the negative electrode to optimize the performance of Ni-MH batteries. It was synthesized applying the sol-gel method and its structural properties were examined using SEM and XRD. Additionally, electrochemical studies using galvanostatic polarization and cyclic voltammetry were performed to investigate some important parameters such as the discharge potential, the exchange current density and the Nernst potential.

By comprehensively analyzing these parameters, the electrochemical behavior of $LaNiO_3$ and its potential as a negative electrode of Ni-MH batteries was thoroughly investigated and deeply understood.

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

The $LaNiO_3$perovskite-type oxide was synthesized using Pechini’s sol-gel method [48-50]which is a process applied to elaborate materials and produce good alloys allowing the synthesis of materials with high homogeneity and purity and used at different temperatures through simple chemical reactions. The utilized precursor materials 1 mole of [La $(NO_3)_3$, $6H_2O$] (purity 99.0%) and [Ni $(NO_3)_2$. $6H_2O$] (purity ≥98%) were completely dissolved. Afterwards, citric acid and ethylene glycol were added to the solution to form a metal complex and obtain a solid solution., respectively. The resulting mixture was homogenized through stirring with a heated magnetic stirrer until a sol (a wet gel) solution was provided. The wet gel was, subsequently, dried for 12 hours at 120°C in an oven, producing powders calcined at 973 K during 5 hours in an oven to form the corresponding phase[51].

2.2. Sample characterization

The sample was structurally and electro-chemically characterized applying several techniques**.** Firstly, a Bruker D8 Advance diffractometer (λCoKα = 1.789 Å) was employed to analyze the structure of the used sample. Then, to examine the morphology of the alloys, a scanning electron microscope (SEM JEOL JSM-5800LV), operating at 30 kV secondary electrons, was used. Then, to determine the chemical composition of the sample, energy dispersive spectroscopy (EDS) was utilized. The working electrode was prepared utilizing the 'latex' technique [52-55]. To achieve the optimum conductivity, 80% of the alloy powder was combined with 10% black carbon, while 10% polytetrafluoroethylene (PTFE) was added to the composition in order to make the electrode more flexible. The resulting LaNiO3 perovskite-type oxide was wetted with ethanol and the obtained paste was rolled out several times with a glass roller until the alcohol evaporated totally. The PTFE was fibrillated by folding and spreading the paste. Finally, two pieces of latex with0.3 mm thickness, were pressed on both sides of the nickel grid acting as current collector [52, 56]. The obtained negative electrode was placed in an open three-electrode cell filled with a 6 M KOH potassium solution in the presence of two other electrodes: a nickel auxiliary electrode and a Hg/HgO reference electrode.

2.3. Electrochemical measurements

All the electrochemical measurements were conducted at 298K using an EC-Lab® V10.12 potentiostat/galvanostat/EIS in a conventional open half-cellput in a thermostatically-controlled water bath. A nickel wire and an Hg/HgO electrode were used as counter and reference electrodes, respectively. The activation process consists in charging and discharging the electrodes at a rate of C/10 for thirty cycles at 298K with a current density of 14.54 mA. g^{-1}during15 hours. Afterward, the electrodes were discharged at the most appropriate discharge potential that gave the best electro-chemical cycling results.

3. RESULTS AND DISCUSSION

3.1.Structural and morphological analysis

To identify the phase of the alloy powder, the peaks positions of the used samples were compared to that used in the reference file(JCPDS file n° 00-033-0710). The diffraction lines were indexed to a perovskite type structure, showing the absence of extra peaks in the $LaNiO_3$ perovskite type oxide. This perovskite, having a cubic crystal structure, was classified under the space group Pm-3m (Fig. 1).

The X-ray diffractograms were refined using the Rietveld method, based on the Pearson crystal structure library and the Maud program. This method consists in fitting the calculated diagram as closely as possible to the measured diagram by identifying the phases present in the powder under examination, as well as their mass proportions and mesh parameters. The Rietveld refinements (Fig. 2) produced an excellent fit outcome, without detecting any secondary phase. In addition, the average crystallite size of the $LaNiO_3$ powder was measured by the Debye-Scherrer method. The latter is based on the phenomenon of constructive interference that occurs when electromagnetic radiation of an appropriate wavelength passes through a crystal material and the wavelength is within the range of the interplanar spacing. In fact, the crystals were diffracted once the Bragg diffraction condition described by Equation 1 was satisfied.

$$2dsin\theta = n\lambda \quad (1)$$

After indexing the powder diagram, the list containing the obtained d_{hkl} values and their intensities I (h k l)was created. Subsequently, the parameters and volume of the mesh were assessed.

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (2)$$

The average crystallite size can be estimated using the Scherrer equation: $D = k\lambda / \beta cos\theta$

$$D = \frac{K\lambda}{\beta cos\theta} \quad (3)$$

where k is the Scherrer constant (set to ~0.9 for spheroidal morphology), λ denotes the wavelength of the incident beam,θis the position of the main peak ($\lambda CoK\alpha$ = 1,789 Å) and β corresponds to the half-height width of the main peak.

The calculated average crystal size and the unit cell volume were equal to 21 nm and 56.66 $Å^3$, respectively. It can be seen, from Figures 1 and 2, that the two used software (X'pert high score and Maud) gave the same results.

Scanning electron microscopy provides information on powder structure and texture, as well as on the size and shape of grains or agglomerates after the calcination stage. Figure 3 shows the SEM image of $LaNiO_3$. From this figure, the particles are of medium size. The granular texture of the powders is made up of the aggregation of different particle sizes and shapes, with an average grain size of no more than 22 µm. The formation of agglomerates is probably due to the nature of the solvent used in sample preparation.

Energy dispersive X-ray spectroscopy (EDS) is generally utilized to analyze the elemental composition of the studied sample. Figure 4 demonstrates the different steps of applying the energy dispersive spectroscopy (EDS) used to analyze the elemental composition of a $LaNiO_3$ nanomaterial.

Table 1 presents the results of the quantitative analysis.

The obtained findings indicate the presence of La, Ni and O in the sample and the absence of additional impurities in its regions. These results suggest that the prepared sample was pure.

3.2. Electrochemical results

3.2.1 Optimization oftheDischarge Potential

Figure 5 illustrates the curves of the discharge of the $LaNiO_3$ perovskite-type oxide electrode at a C/10 discharge rate, at room temperature and for various discharge potentials ranging from -0.4 to 0.5 V.

The maximum discharge capacity at different applied discharge potentials was measured. It did not exceed 10 mAh. g-1at discharge potentials of -0.4 V, -0.3 V and -0.2 V for the 1st and 2nd cycles, respectively. Similarly, the discharge potentials of 0.2 V and 0.3 V gave discharge capacities of around 30 and 56 mAh. g^{-1}during the 1stactivation cycle, respectively, and did not exceed 10 mAh. g^{-1} at the 2nd cycle.

Figure 5 reveals that the highest electrochemical discharge capacities equal to 98 mAh. $g^{-1}$and 89 mAh. g^{-1}, were obtained, respectively, at the 1st and 2nd cycles at a discharge potential of +0.5 V. It was also obvious that the discharge plateau was not defined for negative discharge potentials and the specific absorption region was very small. As a result, the hydrogen uptake kinetics was very low due to the reduction of the reaction zone for the negative range of potential. However, the discharge plateau was easily identifiable at discharge potentials of 0.4 V and 0.5 V, for the 1st and 2nd cycles respectively, because of the increase in the reaction zone that favored the hydrogen absorption and desorption. Thus, the electrochemical discharge potential of +0.5 V was selected to obtain the best cycling results.

3.2.2 The cycling properties of perovskite-type $LaNiO_3$ oxide: Activation, cycling stability and reversibility.

To investigate the charging and discharging behavior of the negative electrode, the chronopotentiometry technique was employed. This method applies a constant current during the charge and discharge cycles and monitors the changes in potential over time. The electrode was initially charged ata C/10 rate. Then, it was discharged at a D/10 rate until achieving the optimal electrochemical discharge potential of 0.5 V vs. Hg/HgO. This process was repeated for 30 cycles at a temperature of 298 K.

Figure 6 illustrates the charge/discharge potentials of the $LaNiO_3$ electrode at C/10 rate and 298K as a function of time.

It is worth noting that the charge curves exhibit a long potential plateau due to the stable chemical bonds formed between the perovskite oxides and the protons. In Figure 5, the second cycle demonstrates a rapid activation indicating a better reversibility of the charge/discharge reaction at the negative electrode surface.

The first cycle of the $LaNiO_3$ electrode at an optimal discharge potential equal to 0.5 V resulted in a discharge capacity of approximately 18 mAh. g^{-1}. Subsequently, the discharge capacity attainedits highestvalue of 119 mAh. g^{-1}during the 2nd cycle. However, the discharge capacity gradually decreased during subsequent cycles and eventually stabilized at 22 mAh. g^{-1}. This result suggests that the activation process of the $LaNiO_3$ electrode was rapid; it required only two activation cycles to reach its stable discharge capacity. After being activated, the electrochemical discharge capacity decreased significantly, revealing the beginning of the degradation of the elctrode performance caused by theoxidation of the material active surface. This process led to thereduction of the oxide electrode’s electro-active surface during cycling.

It is important to highlight that, although many studies proved that the use of perovskites as negative electrodes ofNi-MH batteries may cause a sudden decrease in electrochemical discharge capacity [57, 58], hydrogen insertioninto the sites of the employed electrode produced favorable energetic efficiency.

Fig. 7shows the evolution of the discharge capacity as a function of the number of cycles.

The reproducibility of the utilized was examined by conducting two tests under the same experimental conditions employing two $LaNiO_3$ electrodes produced by the same sol gel method.

The obtained results demonstrate that, in the two performed tests, thedischarge capacity evolved in the same way. In fact, the first testshows that the activation of the electrode during the second cycle provided an electrochemical capacity equal to 120 mAh. g^{-1}, while the secondone reveals that the activation during the third cycle gave an electromechanical capacity equal to 130 mAh. g^{-1}.

Both experiments illustrate a similar decrease in the electrochemical discharge capacity over cyclying, which provides further evidence that the perovskite type electrode is highly reproducible.

The half-charge and half-discharge potentials as well as the polarization of the perovskite-type oxide $LaNiO_3$ electrode were studied during twenty activation cycles under optimal discharge potential conditions of 0.5 V, C/10 rate and temperature of 298K. Figs. 8 and 9 display the variation of these parameters as a function of the number of cycles. More precisely, Figure 8 illustrates the half-charge and half-discharge potentials, while Fig.9 presents the polarization curves.

During the activation process, the half-discharge potential of the electrode shifted towards more positive values, which facilitated the insertion of hydrogen into the electrode. The obtained value of the half-discharge potential at activation, varying between 0.43 and 0.45 V during the first three activation cycles, was likely due to the high discharge capacity. However, as the activation proceeded, the half-discharge potential became less positive, which made it difficult to insert hydrogen into the interstitial sites of the used electrodes, until it stabilized towards the end of cycling at approximately 0.22 V.

The first polarization values, representing the potential difference between the half-charge and half-discharge, were approximately equal to 107 mV during the first cycle. This value gradually increased to 185 mV at the seventh cycle before stabilizing at 170 mV during the remaining cycles. The first attenuation of the polarization observed during the first cycles can be attributed to the expansion of the active surface of the $LaNiO_3$ electrode.

Notably, these findings correlate with the electrochemical discharge capacity results which suggest that the hydrogen absorption/desorption reaction in the sites was more reversible during the initial cycles.

The evolution of the discharge capacity of the $LaNiO_3$ perovskite oxide electrode is illustrated in Fig. 10. The electrode was tested under optimum conditions: discharge potential of 0.5 V, discharge rate equal to C/10 and temperature of 298K.

During activation, the discharge capacity increased with the rise in the number of cycles to reach its maximum value. Indeed, at the first cycle, the discharge capacity was about 18 mAh. g^{-1}. Then, it evolved to reach its maximum value of about 120 mAh. g^{-1} at the 2nd activation cycle under an optimum discharge potential of 0.5 V and at C/10 rate.

It was clear that the electrochemical discharge capacity increased with the activation of the used electrode, which allowed the absorption of hydrogen in the interstitial sites [58].

After the activation of the electrode, the discharge capacity declined before stabilizing at around 22 mAh. g^{-1} after along cycling. During this process, the capacity decreased by approximately 18%.

The discharge capacity of a Ni-MH electrode degraded due to various factors such as the formation of a passivation layer on the electrode surface. This layer impeded the occurrence of the electrochemical reactions that facilitated the functioning of the battery. It was formed by the accumulation of impurities at the electrode surface, the degradation of the electrode material [59]

Another factor that may reduce the discharge capacity of Ni-MH is the loss of the active material caused by overcharging, undercharging or the exposure of the electrode to high temperature. Moreover, the repeated cycling can modify or degrade the interstitial sites of the electrode.

Overall, the decrease of capacity during cycling depends on various factors including the composition and structure of the Ni-MH electrode, the operating conditions of the battery and the type of the applied cycling protocol.

As demonstrated in the literature [60], the discharge capacity of the electrode used in the present work after activation decreased considerably, as it is the case for $LaFeO_3$ which was synthesized through a stearic acid combustion process, and $LaGaO_3$ prepared via the sol-gel method.

To investigate the reproducibility of the negative electrode, a second electrochemical cycling was performed and the discharge capacity was studied over 20 cycles.

3.2.3. Cyclic voltammetry

The voltammograms were analyzed using software (Origin) to plot the potentiodynamic polarization or the Tafel curves. Figure 11 displays the progression of the Tafel curves of the $LaNiO_3$ electrode at scan rate equal to1mV.s^{-1} and temperature of 25°C. The corresponding experimental data were matched to those provided by the theoretical model depicted by the Butler-Volmer equation to obtain both the current density and Nernst potential values. Equation (3), where I_0, E_0, b_c, and b_a represent, respectively, the current density, the Nernst potential and the Tafel constants, was applied to describe the experimental data[61, 62]:

$$I= I_0 \{\exp [b_a(E-E_0)]-\exp [b_c(E-E_0)]\} \qquad (3)$$

The obtained results show a good accordance between the experimental data and calculated values, which validates the reversibility of the hydrogen absorption-desorption kinetics at the electrode surface.

As exposed in Fig. 11, during the first activation cycles, all the Tafel curves shift slightly towards the lowest potential values that decrease at the end of the cycling.

Figure 12 reveals that the exchanged current density of the $LaNiO_3$ negative electrode increases during the initial charging/discharging cycles. It reaches its highest value at 0.22 A/g during the 4th cycle, indicating improved absorption kinetics approaching activation**.** This increase was attributed to both the rapid hydrogen adsorption process at the electrolyte-electrode interface and the expansion of the active surface. This process became faster approaching activation. However, after activation, the exchange current density decreased and, then, it stabilized at about 0.025 A $.g^{-1}$. This decline can be explained by the fact that the electrode structure was modified by cycling which reduced the number of interstitial hydrogen absorption sites[38]. These findings are in good accordance with those obtained by the galvanostatic method. It is worth noting that, in the performed experiments, this evolution trend of the exchange current density was observed in perovskite-based negative electrodes [63,64].Although both intermetallic compounds and perovskite compounds can be used as the negative electrodes of Ni-MH batteries, they have different current densities.

More precisely, intermetallic compounds have a relatively low current density which reflects low charge and discharge rate. However, perovskite compounds have high current density resulting in faster charge and discharge rate. This characteristic makes perovskite compounds more efficiently employed in applications that require high charge and discharge rate.

Figure 13 shows the evolution of the Nernst potential of the $LaNiO_3$ perovskite electrode during electro-chemical cycling process.

The Nernst equation allows determining the evolution of exchange of the current density and Nernst potential. In a Ni-MH battery, the negative electrode is typically made of hydrogen-absorbing metal alloys and the electrochemical reaction involves the reversible absorption and desorption of hydrogen ions (H^+) and electrons (e^-) to form hydrogen gas (H_2) and metal hydrides (MH_x). Generally, the Nernst potential of the negative electrode is influenced by several factors including temperature, the mobility of hydrogen ions in the electrolyte as well as the composition and morphology of the electrode material.

During the first charging/discharging cycles, this parameter evolved towards more negative potential values to reach its minimum of approximately -350 mV during the fourth cycle. After activation, the Nernst potential value increased towards more positive potential values to attain an oscillating value almost equal to 50 mV towards the end of the cycling process.

It was clearly observed that the electrochemical performance of the electrode improved with the rise of temperature from 298K to 333K[37, 65-67]for the perovskites, specifically in terms of the electrochemical capacity and activation.

3.2.4. Electrochemical impedance spectroscopy

In the conducted experiments, EIS was used to study the $LaNiO_3$ electrode/electrolyte interface phenomena.

The Nyquist diagrams of the $LaNiO_3$ negative electrode for different cycles are shown in Fig. 14.

The obtained diagrams consist of three regions:

-A small semi-circle in the high frequency region (resulted from the charge-transfer process occurring at the interface).

- A large incomplete semi-circle in the low frequency region. It represents the electrode-surface processes (adsorption/absorption).
- A linear section in the mid-frequency region, inserted between the two semicircles and inclined at about 45° to the real axis. It was associated with the Warburg impedance.

The model used to fit the experimental data is $R_S(Q_{dl}R_{ct}(Q_{ad}(R_{ad}(WR_{ab}))))$where R_s is the electrolyte resistance, R_{ad} denotes the hydrogen adsorption resistance, R_{ct} corresponds to the charge transfer resistance, R_{ab} represents the hydrogen absorption resistance and W designates the Warburg impedance.

This equivalent circuit resembles to that employed in our previous research work on AB5-type and oxides alloys [40-43]. It was utilized to characterize the impedance spectra collected under various temperatures, potentials and cycling conditions [40-43].

The inclusion of the constant phase element (referred to as Q, equivalent to CPE) and its corresponding impedance was justified by the depression of the semi-circular response due to the material porosity, inhomogeneity and roughness of the electrode surface.

$$Z_{CPE} = \frac{1}{Y_{CPE}(j\omega)^n} \quad (4)$$

The two parameters (YCPE and n) represent the admittance and the exponent parameter different to unity, respectively.

In order to accommodate the phenomenon of the semi-infinite hydrogen atom diffusion within the the electrode, the Warburg element (W) was incorporated into the proposed electrical model.

$$Z_W = \frac{\delta}{\sqrt{\omega}}(1 - j) = \frac{1}{\sqrt{\omega}\ Y_0\sqrt{2}}(1 - j) \quad (5)$$

where ω denotes frequency, j represents the square root of -1, d stands for the experimentally-determined Warburg coefficient and Y_0 corresponds to the Warburg admittance.

Y_0 can be either deduced from fitting EIS Nyquist curves or expressed as a function of δ:

$$Y_0 = \frac{1}{\delta\sqrt{2}} \quad (6)$$

This circuit configuration summarizes our previous work [41-42]and allows interpreting the impedance behavior under various conditions and accommodating effects such as porosity and hydrogen diffusion in the electrode.

The modeling process was performed iteratively to evaluate the suitability of a given model to interpret experimental data. It involved using both the chi-squared (χ2) value obtained by the electrical model electrical model and the percentage error values provided by each component of the circuit. The expression used to calculate the value of $\chi^2$is written below [68]:

$$\chi^2 = \sum_{i=1}^{i=n} [W_i^{'}(Z_{i,exp}^{'} - Z_{i,cal}^{'}(\omega_i, \bar{p})^2 + W_i^{"}(Z_{i,exp}^{"} - Z_{i,cal}^{"}(\omega_i, \bar{p}))^2] \qquad (7)$$

where ($Z'_{i,exp}$) ($Z\ '_{i,cal}$) ($Z''_{i,exp}$) ($Z''_{i,cal}$) are the experimental (calculated) real and imaginary parts of the impedance ;W'_i and W''_I designate the statistical weighting data; and n is the number of data points.

The χ^2 value was minimized by correlating the experimental points to the theoretical data points. This iteration process was conducted by determining the differences between the experimental and determined data points. The discrepancies were, then, squared so that larger disparities would be more important. All these differences were combined and, subsequently, separated by a weighting element. According to the literature, a χ^2 of around 10^{-3} or less is a χ2 of around 10^{-3} or below was acceptable for a given model.

The various parameter values presented in the above-presented Nyquist diagrams determined by the ZSimpWin software are presented in Table 2.

Based these values, the change of some parameters as a function of cycling was determined. Figures 15, 16 and 17 depict the evolution of the following parameters (R_{ct}, C_{dl}, C_{ad}, R_{ad}, I_0 and D_H) as a function of cycling.

It can be seen, from Figures15 and 16, that the resistance of the charge transfer and that of adsorption evolve in the same direction. In fact, it is clear that the charge transfer resistance decreases from 43 $\Omega.cm^2$ before cycling, to 11 $\Omega.cm^2$ towards the end of the cycling process. However, the resistance decreases from 105 $\Omega.cm^2$ to 18 $\Omega.cm^2$ during the 30th charging/discharging cycle. As far as the double layer and adsorption capacities of the $LaNiO_3$ electrode are concerned, both of them rise as the number of cycles increases.

Figure 17 illustrates the evolutions in the current density and hydrogen diffusion coefficient values of the LaNiO3 negative electrode during cycling.

As demonstrated in Fig. 17, I_0 of the $LaNiO_3$ electrode increases from 9 mA/g (cycle 0) to 45 mA/g as the number of cycles rises, indicating a rapid process of hydrogen adsorption at the $LaNiO_3$/electrolyte interface. This finding is inversely proportional to the charge-transfer resistance whose value decreases as the exchange current density increases. By augmenting the number of the cycles , the $LaNiO_3$ powder under went microcracking, resulting in the pulverization of the powder into micrometer-sized particles due to the expansion of the crystal cell caused by hydrogen absorption and desorption [69]. It was also obvious that microcracking increased the reaction surface area and improved the activation of H adsorption at the electrode/electrolyte interface and, therefore, enhanced the hydrogen exchange current density. Consequently, the microcracking activation.

The investigation of the impact of cycling on the $LaNiO_3$ negative electrode revealed an intriguing pattern in the evolution of the hydrogen diffusion coefficient value which initially rose to reach its peak at around the 20thcycle.However, beyond this peak, the diffusion coefficient started to decline to attain its minimum at the 30th cycle. This observation suggests that cycling generally affects the ability of hydrogen atoms to diffuse within the electrode material.

The initial increase of the hydrogen diffusion coefficient value might be attributed to certain electrochemical or structural changes on the electrode surface induced by cycling. Subsequently, the decrease of the hydrogen diffusion coefficient value could impede or limit the diffusion process, possibly due to the degradation of the used material, the altered electrochemical properties or the accumulation of the oxides films at the electrode surface. Overall, this finding highlights the intricate interplay between the cycling process and hydrogen diffusion dynamics in the negative electrode of Ni-MH battery.

4. CONCLUSION

In this work, the electrochemical properties of $LaNiO_3$, an anode material used innickel-metal-hydride battery applications, were investigated.Thestudiedcompound was synthesized using a simple and inexpensive sol-gel method. The structural analysis showed thatit crystallized in the rhombohedral lattice without the appearance of any secondary crystallographic phase. The $LaNiO_3$ electrode was quickly activated in only two cycles and achieved itsmaximum discharge capacity of 119 mAh. g^{-1}at 298K. The decrease in the discharge capacity after activation could be attributed to a decrease in the interstitial sites or catalytic activity of the electrode. Throughout the cycles, a good correlation was observed between the evolution of the electrochemical discharge capacities and that of the polarization and exchange current density.The EIS analysis highlighted thatthe electrochemical behavior of the oxide-based electrode was primarily influenced by the chargetransfer rate and the real electrode surface. Notably, the highest values of the kinetic parameterswere obtained after the activation process, providing evidence that the electrochemicalperformance of this oxide-type electrode improved during the electrochemical activation.

These findings indicate that $LaNiO_3$ exhibited promising potential as an anode material for nickel-metal-hydride batteries.

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