Electrochemical properties of perovskite-type oxide $LaNiO_3$ for application as active material for nickel–metal hydride battery anode

Ahmed khedimallah[a], Wissem Zayani[a], Youssef Dabaki[a,b], Abbes Kaabi[a], Chokri Khaldi[a], Jilani Lamloumi[a], Michel Molière[c], Omar El-Kedim[d], Nouredine Fenineche[c],

[a]Université de Tunis, ENSIT, LR99ES05, 1008, Montfleury, Tunisia
[b]Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France.
[b]ICB-PMDM/FR FCLAB, UTBM, UBFC, 90010, Belfort Cedex, France
[c]FEMTO-ST, MN2S, UTBM, UBFC, 90010, Belfort Cedex, France

Abstract—In this study, the hydrogen storage properties of $LaNiO_3$, a perovskite-type oxide that is commonly used as a negative electrode in nickel-metal hydride batteries, were investigated. The $LaNiO_3$ sample was synthesized using the sol-gel method and its structure and electrochemical characteristics were systematically examined. X-ray diffraction analysis confirmed that the $LaNiO_3$ material consists of a single phase and crystallizes in the cubic space group Pm-3m. To evaluate its electrochemical performance, electrochemical measurements at 298K using chronopotentiometry, cyclic voltammetry, and Electrochemical Impedance Spectroscopy techniques were conducted. Overall, this study provides valuable insights into the hydrogen storage behavior of $LaNiO_3$ alloy, which can be useful for developing high-performance nickel-metal hydride batteries.

Keywords –perovskite$LaNiO_3$ type oxide; Nickel metal hydride accumulators; Galvanostatic charge and discharge; Electrochemical properties, Discharge capacity, the cyclic voltammetry method and Electrochemical impedance spectroscopy.

1. INTRODUCTION

The increasing demand for battery technologies that are both efficient and dependable has generated a surge of interest in exploring novel materials for their development [1-4]. In the past two centuries, the battery market has nearly doubled, mainly due to the rise of mobile applications such as cell phones, tablets, and laptops. Today, the growth of electric and hybrid, vehicles is driving the demand for improved battery technology. As a result, significant effort has been dedicated into identifying new materials for Ni-MH battery technology that can offer hydrogen storage capabilities in various operating circumstances [5-8]. The Ni-MH battery [9-14] is considered a crucial component for various applications such as photoelectricity and electronics [15, 16], the medical field, solar cells, and the next generation of hybrid or fully electric vehicles. However, this technology is still relatively new and has great potential for improvement. Reaching its full potential requires optimizing the negative electrode by developing new, less expensive materials with satisfactory capacities, quick and sustainable charging and discharging, and stability throughout the cycles [17-23]. Recent studies have explored the use of ABO_3 perovskite-type oxides, which exhibit superior hydrogen absorption properties [24-27]. Several works have evaluated their electrochemical performance, including studies by G. Deng and colleagues [28, 29], who prepared a $LaFeO_3$ alloy using a stearic acid combustion method, achieving a discharge capacity of 80 $mAhg^{-1}$ at 298K. They also used the same method to prepare the $LaCrO_3$ alloy, which had an electrochemical discharge capacity of 194.8 $mAhg^{-1}$. Q. Wang fabricated the $LaFeO_3$ alloy [30] using a similar method, achieving an electrochemical discharge capacity of 143.3 at 298K. The perovskite-type oxide $LaNiO_3$ is an innovative material with various applications, such as electrocatalysis[31], superconductivity [32], rechargeable zinc-air batteries [33], lithium-oxygen batteries [34], $Li\text{-}O_2$ batteries [35] and as active material for Ni-MH accumulators. This is due to its advantages, such as the simplicity of synthesis and good electrochemical behavior at different temperatures. However, previous studies have shown that perovskites have a low electrochemical discharge capacity at 25°C [36-38]. Therefore, this study aims to analyze this problem and propose a solution.

To optimize the performance of Ni-MH batteries, perovskite-type oxide $LaNiO_3$ alloy was selected as the negative electrode. It was synthesized using the sol-gel method and the corresponding structural properties were studied using SEM and XRD. Additionally, electrochemical studies using galvanostatic polarization and cyclic voltammetry were performed to examine important factors such as discharge potential, exchange current density and the Nernst potential.

By comprehensively analyzing these parameters, a better understanding of the electrochemical behavior of $LaNiO_3$ and its potential as a negative electrode material for NI-MH batteries was gained.

2. EXPERIMENTAL

2.1. Sample preparation

The $LaNiO_3$ perovskite-type oxide was synthesized using Pechini's sol-gel method [39-41], a technique that enables the oxides powder through simple chemical reactions. The precursor materials used were 1 mole of [La $(NO_3)_3$, $6H_2O$] and [Ni $(NO_3)_2$. $6H_2O$], which were completely dissolved. Citric acid was added to form a metal complex, followed by the addition of ethylene glycol to obtain a solid solution. The resulting mixture was homogenized through stirring with a heated magnetic stirrer until a sol (a wet gel) solution was obtained. The wet gel was then dried for 12 hours at 120°C in an oven, resulting in powders that were calcined at 973 K for 5 hours in an oven to form the corresponding phase [42].

2.2. Sample characterization

The sample was subjected to various analytical techniques for comprehensive characterization. Firstly, a Bruker D8 Advance diffractometer ($\lambda CoK\alpha$ = 1.789 Å) was employed to perform a structural analysis. To examine the morphology of the alloys, a scanning electron microscope (SEM JEOL JSM-5800LV) was used, operating at 30 kV secondary electrons. Additionally, to determine the constituents' content and composition of the alloys, energy dispersive spectroscopy (EDS) was utilized.

The working electrode's alloy was synthesized using the "Latex" technique [43-46]. To achieve optimum conductivity, 80% of the alloy powder was combined with 10% black carbon, while 10% of polytetrafluoroethylene (PTFE) was added to provide flexibility to the electrode. The resulting perovskite-type oxide $LaNiO_3$ was utilized. To form the electrode, two pieces of this latex measuring 0.5 cm^2 each were pressed onto both sides of a nickel grid utilized as a current collector [43, 47].

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-cell, which was placed 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 involved 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} for 15 hours. Afterward, the electrodes were discharged at the most appropriate discharge potential based on a precise experimental study.

3. RESULTS AND DISCUSSION

3.1. Microstructure analysis

To identify the phase of the alloy powder, the measured values were compared to the indexed values from the reference file (JCPDS file n° 00-033-0710), prioritizing the d_{hkl} values with the strongest intensities. Indexing a diffraction pattern require determining which reflection corresponds to which planes. Once the powder pattern was indexed, a list of d_{hkl} values that were observed along with their corresponding intensities (I_{hkl}) is generated. This enables the accurate assessment of both the unit cell parameters and the unit cell volume. The diffraction lines were indexed to a perovskite type structure, confirming the absence of any extra peaks in the $LaNiO_3$ perovskite type oxide, indicating the efficiency of the method of preparation used. This perovskite has a cubic crystal structure and is classified under the space group Pm-3m (Fig. 1).

The Match 3 software was employed to fine-tune the experimental X-ray diffraction (XRD) spectra of $LaNiO_3$ powder and confirm its cubic perovskite structure, with a Pm-3m space group. The Rietveld refinements (Fig. 2) produced an excellent fit outcome, without any secondary phase detected. Furthermore, the average crystallite size of the $LaNiO_3$ powder was calculated to be 21 nm, and its unit cell volume was found to be 56.66 $Å^3$.

It can be seen at this level that the two softwares used (X'pert highscore and Match3) gave the same result.

The scanning electron microscope (SEM) is a highly effective instrument for analyzing surface features of samples, providing valuable information on the structure, texture, and grain size of powders following calcination. The powder's morphology and grain size were closely examined, as demonstrated in Fig. 3, which depicts the SEM image of the oxide powder. The image reveals that the particles have a medium grain size and a granular texture that arises from the accumulation of particles with varying sizes and shapes. The average grain size, $D_g = 22\mu m$, indicates that the alloy has a homogeneous and dense structure.

Energy dispersive X-ray spectroscopy (EDS) is a valuable technique that enables users to analyze the elemental composition of a given sample accurately. Fig. 4 demonstrates the application of energy dispersive spectroscopy (EDS) to analyze the elemental composition of a $LaNiO_3$ nanomaterial, indicating the presence of La, Ni, and O in the sample without any additional impurities. These findings suggest that the prepared sample is pure. Additionally, the analysis reveals that the elements tend to disperse in specific regions.

Table 1 presents the results of the quantitative analysis conducted on the chosen area.

3.2. Electrochemical results

3.2.1 Optimization of Discharge Potential for Maximum Discharge Capacity

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

The maximum discharge capacity at different applied discharge potentials was measured and found to be 5, 6 and 6 mAh g^{-1} at discharge potentials of -0.4 V, -0.3 V and -0.2 V respectively. Similarly, discharge potentials of 0.2 V and 0.3 V yielded discharge capacities of about 9 and 10 mAh g^{-1} respectively (Activation). The discharge curves exhibited changes with varying applied discharge potential (+0.4 V), with the highest electrochemical discharge capacity of 61 mAh g^{-1} observed at a discharge potential of +0.5 V. Notably, the discharge plateau was not defined for negative discharge potentials, and the specific absorption area was very small. Consequently, the hydrogen absorption kinetics was very low due to the small reaction zone. In contrast, the discharge plateau was easily distinguishable for discharge potentials of 0.4 V and 0.5 V, which could be attributed to an increase in the reaction zone that favors hydrogen absorption and desorption. Thus, the electrochemical discharge potential of +0.5 V was selected, which exhibited the highest electrochemical discharge capacity, as the optimal applied discharge potential for these measurements.

3.2.2 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 involves applying a constant current during the charge and discharge cycles and monitoring the changes in potential over time. The electrode was initially charged using a C/10 rate, followed by discharge at a D/10 rate until an optimal electrochemical discharge potential of 0.5 V vs. Hg/HgO was achieved. This process was repeated for 30 cycles at a temperature of 298 K (25°C).

Fig. 6 illustrates the charge/discharge potentials at C/10 rate and 25°C as a function of time for the $LaNiO_3$ electrode.

It is worth noting that the charge curves exhibit a prolonged and level potential plateau, which can be attributed to the stable chemical bonds formed between the perovskite oxides and protons. In Figure 5, the second cycle demonstrates a rapid activation, indicating a highly preferred discharge time that reflects the reversibility of the charge/discharge reaction on the negative electrode surface.

The first cycle of the $LaNiO_3$ electrode at an optimal discharge potential of 0.5 V resulted in a discharge capacity of approximately 18 $mAhg^{-1}$. Subsequently, the discharge capacity increased to its peak value of 119 $mAhg^{-1}$ during the 2nd cycle. However, the discharge capacity gradually decreased over subsequent cycles and eventually stabilized at 22 $mAhg^{-1}$. This suggests that the activation process of the $LaNiO_3$ electrode is rapid, requiring only two cycles to reach its stable discharge capacity. After being activated, the electrochemical discharge capacity has significantly decreased, indicating the start of a degradation process caused by oxidation on the active material surface. This process results in a reduction of the oxide electrode's electroactive surface during cycling.

It is important to highlight that although many studies using perovskites as negative electrodes for Ni-MH batteries have shown a sudden decrease in electrochemical discharge capacity [48, 49], the results demonstrate favorable energetic efficiency and a reversible reaction regarding hydrogen insertion .

The half-charge and half-discharge potentials, as well as the polarization, of the perovskite-type oxide $LaNiO_3$ electrode were studied over twenty cycles under optimal discharge potential conditions of 0.5 V, a C/10 rate, and a temperature of 25°C. Fig. 7 and Fig. 8 display the variations of these parameters as a function of the number of cycles. Specifically, Figure 7 shows the half-charge and half-discharge potentials, while Figure 8 shows the polarization.

During the activation process, the half-discharge potential of the electrode shifts towards more positive values, which in turn facilitates the insertion of hydrogen into the electrode. Specifically, the value of the half-discharge potential at activation is around 0.43-0.45 V during the first three cycles, likely due to the higher discharge capacity at this stage. However, as the activation proceeds, the half-discharge potential becomes less positive, which makes it increasingly difficult to insert hydrogen, until it stabilizes towards the end of cycling at approximately 0.22 V.

The first polarization values, representing the potential difference between half-charge and half-discharge, measures approximately 107 mV during the first cycle. This value gradually increases to 185 mV at the seventh cycle, before eventually stabilizing at 170 mV for the remaining cycles. The first attenuation of the polarization observed during the first few 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 reaction is more reversible during the initial cycles.

The discharge capacity evolution of the $LaNiO_3$ perovskite oxide electrode is shown in Fig. 9. The electrode was tested under optimum conditions, including a discharge potential of 0.5 V, a discharge rate of C/10 and a temperature of 25°C.

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

The increase of the electrochemical discharge capacity is explained by the activation process of our electrode which is explained by the increase of the specific surface of our alloy allowing the absorption of hydrogen in the interstitial sites[49].

Following its activation, the discharge capacity experiences a decline before eventually reaching stability at around 22 $mAhg^{-1}$ after along cycling. During this process, the capacity decreases by approximately 18%.

During cycling, the discharge capacity of a Ni-MH electrode can decrease due to various factors. One such factor is the formation of a passivation layer on the electrode surface, which can impede electrochemical reactions necessary for the battery to function. This layer can result from the accumulation of impurities, the degradation of the electrode material, and unwanted reactions at the electrode surface [50]. Another factor is the loss of active material, which can occur due to overcharging, undercharging, and exposure to high temperatures. Side reactions at the electrode surface during cycling, such as the oxidation of the electrolyte or the reduction of oxygen, can also reduce capacity. Repeated cycling can cause structural degradation, leading to a decrease in capacity. This can be caused by mechanical stress, thermal stress, and chemical degradation. The specific cause of capacity loss during cycling can depend on various factors, including the composition and structure of the Ni-MH electrode, the operating conditions of the battery, and the specific cycling protocol used.

The observed reduction in discharge capacity following activation is consistent with findings on $LaFeO_3$ [28], which was synthesized through a stearic acid combustion process, and $LaGaO_3$, prepared via the sol-gel method [51].

Repeating an experiment is a fundamental aspect of scientific research that helps to ensure the reliability and validity of results. When an experiment is repeated and produces the same outcome, it lends support to the original findings and increases confidence in their accuracy.

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

Fig. 10 illustrates the results of this study, showing the discharge capacity as a function of the number of cycles. Notably, the same trend was observed in the evolution of the negative electrode during this second cycling, providing further evidence that the perovskite-type electrode is highly reproducible.

3.2.3. Cyclic voltammetry

The voltammograms were analyzed using software (Origin) to plot the potentiodynamic polarization or Tafel curves. Fig. 11 displays the progression of Tafel curves of the $LaNiO_3$ electrode at a scan rate of $1 mV.s^{-1}$ and a temperature of 25°C. The corresponding experimental data were matched to the theoretical model depicted by the Butler-Volmer equation to obtain both current density and Nernst potential values. Equation (3) was used to describe the experimental data, where I_0, E_0, b_c, and b_a represent the current density, Nernst potential, and Tafel constants, respectively [52, 53]:

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

The founded fitted results show a good accordance between the experimental and calculated data thereby validating the reversibility of the hydrogen absorption-desorption kinetics at the electrode surface.

All the Tafel curves shift slightly towards the lowest potential during the first activation cycles. Close to the end of the cycling, a return of the potential value towards the highest values is observed.

Fig. 12 indicates that the exchanged current density of the $LaNiO_3$ negative electrode increases during the initial cycles, reaching 0.22 A/g during the 4th cycle, indicating improved absorption kinetics near the activation. This increase is attributed to both the rapid hydrogen adsorption process at the electrolyte-electrode interface and the expansion of the active surface, which becomes faster around activation. However, after activation, a rapid decrease in the exchange current density is observed, stabilizing at about $0.025 A g^{-1}$. This decrease can be explained by the fact that cycling the electrode causes a scouring of its surface, leading to a reduced number of interstitial hydrogen absorption sites [29]. These findings are in line with the results of the galvanostatic method. It's worth noting that this evolution trend of the exchange current density has been widely observed for perovskite-based negative electrodes [54, 55]. Intermetallic compounds and perovskite compounds both have the potential to be used as negative electrodes for Ni-MH batteries, but the rate of current density evolution differs between the two.

Intermetallic compounds have a relatively low current density evolution, which means that the rate of charge and discharge is also slower. On the other hand, perovskite compounds have higher current density evolution, allowing for a faster rate of charge and discharge. This makes perovskite compounds better suited for applications that require a faster rate of charge and discharge.

Fig. 13 shows the evolution of the Nernst potential of the $LaNiO_3$ perovskite electrode during cycle.

The Nernst equation relates the electrode potential to the activities (or concentrations) of the species involved in the electrochemical reaction taking place at the electrode surface. In the case of 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). The Nernst potential of the negative electrode depends on several factors, including the temperature, the activity of hydrogen ions in the electrolyte, the composition and morphology of the electrode material.

During the first cycles, this parameter evolves towards more negative potential values to reach minimum values of approximately -350 mV (fourth cycle). This is probably a sign of the activation phenomenon. After activation, a re-increase of the Nernst potential value towards more positive potential values is observed to reach an oscillating value of approximately 50 mV towards the end of the cycling.

It was clearly observed that the change of temperature from 25°C to 60°C [29, 56-58] for the perovskites will lead to an improvement of the electrochemical performance in terms of electrochemical capacity and activation which will take place in the next work.

3.2.4. Electrochemical impedance spectroscopy

In the present work EIS was used to understand 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), dependent on cycling. A large incomplete semi-circle in the low frequency region remaining constant regardless of cycling (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, associated with the Warburg impedance.

The used model 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} is the hydrogen adsorption resistance, R_{ct} is the charge transfer resistance, R_{ab} is the hydrogen absorption resistance and W is the Warburg impedance.

The process of modeling was performed iteratively to evaluate the suitability of a given model for the experimental data. This involved using both the value of chi-squared (χ2) for the overall model and the percentage error values for each component of the circuit. The expression used to calculate the value of χ^2 was [59]:

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

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 are the statistical weighting data , and n is the number of data points.

When correlating the experimental points to the theoretical data points, the χ^2 value was minimized. This was conducted by determining the gap between the experimental and determined data points. The discrepancy was then squared so larger disparities would have a higher importance. All these discrepancies were combined and then separated by a weighting element. According to the literature, a χ^2 of around 10^{-3} or lesser was satisfactory for a given model.

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

The above table allowed the determination of the evolution of some parameters as a function of cycling. In figures 15, 16 and 17 the evolution of the different parameters (R_{ct}, C_{dl}, C_{ad}, R_{ad}, I_0 and D_H) as a function of cycling was presented.

It can be seen on figs. 15 and 16 that the charge transfer resistance and the adsorption resistance have the same evolution trend (the charge transfer resistance decreases from 43 $\Omega.cm^2$ before cycling to 11 $\Omega.cm^2$ towards the end of the cycling while the resistance decreases from 105 $\Omega.cm^2$ to 18 $\Omega.cm^2$ during the 30th cycle). For the double layer and adsorption capacities of the $LaNiO_3$ electrode we can notice that these two parameters evolve in the same way by becoming very important as the number of cycles increases.

As shown in Fig. 17, I_0 of the $LaNiO_3$ electrode increases from 9 mA/g (cycle 0) to 45 mA/g as the cycle number increases, indicating a rapid process of hydrogen adsorption at the $LaNiO_3$/electrolyte interface. This is inversely proportional to the charge-transfer resistance, the value of which is decreased as the exchange current density increases. By increasing the cycle number, the $LaNiO_3$ powder will undergo 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 [60]. This microcracking increases the reaction surface area and improves the activation of H adsorption at the electrode/electrolyte interface. Consequently, the microcracking activation, which is a result of both an increased reaction surface area and an improved electrode surface activation, increases the hydrogen exchange current density.

For the evolution of the hydrogen diffusion coefficient, an increase in its value is observed, which reaches its maximum during the 20th cycle, and then it undergoes a decrease.

4. CONCLUSION

This study investigated the electrochemical properties of $LaNiO_3$ as an anode material for nickel-metal-hydride battery applications. The structural analysis confirmed that the compound was synthesized using a simple and inexpensive sol-gel method and crystallizes in the rhombohedral lattice without the appearance of any secondary phases. The $LaNiO_3$ electrode was quickly activated in only two cycles and achieved a maximum discharge capacity of 119 $mAhg^{-1}$ at 25°C. The decrease in capacity after activation could be attributed to a decrease in 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 those of the polarization and exchange current density. The EIS analysis highlighted that the electrochemical behavior of the oxide-based electrode is primarily influenced by the charge transfer rate and the real electrode surface. Notably, the highest values of the kinetic parameters were observed after the activation process, providing evidence that the electrochemical performance of this oxide-type electrode improves during the electrochemical activation.

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

References

[1] X. Fan, B. Liu, J. Liu, J. Ding, X. Han, Y. Deng, X. Lv, Y. Xie, B. Chen, W. Hu, Battery technologies for grid-level large-scale electrical energy storage, Trans. Tianjin Univ. 26 (2020) 92-103.

[2] X. Zeng, M. Li, D. Abd El-Hady, W. Alshitari, A.S. Al-Bogami, J. Lu, K. Amine, Commercialization of lithium battery technologies for electric vehicles, Adv. Energy Mater. 9 (2019) 1900161.

[3] A. Malhotra, B. Battke, M. Beuse, A. Stephan, T. Schmidt, Use cases for stationary battery technologies: A review of the literature and existing projects, Renewable Sustainable Energy Rev. 56 (2016) 705-721.

[4] M. Abdelbaky, J.R. Peeters, W. Dewulf, On the influence of second use, future battery technologies, and battery lifetime on the maximum recycled content of future electric vehicle batteries in Europe, Waste Manage. (Oxford).125 (2021) 1-9.

[5] W. Zayani, S. Azizi, K.S. El-Nasser, I.O. Ali, H. Mathlouthi, Structural and electrochemical characterization of new co-doped spinel ferrite nanomaterial used as negative electrode in Ni/MH battery, in: 2018 9th International Renewable Energy Congress (IREC), IEEE. 2018, pp. 1-5.

[6] W. Zayani, S. Azizi, M. Salah, K.S. El-Nasser, I. Othman Ali, J. Lamloumi, Structure and electrochemical hydrogen storage properties of Spinel Ferrites $Sm_xZn_{1-x}Fe_2O_4$ alloys (x= 0, x= 0.2, x= 0.4 and x= 0.6) for Ni-MH accumulator applications, Environ. Prog. Sustain. (2022) e14050.

[7] Y. Dabaki, C. Khaldi, O. ElKedim, N. Fenineche, J. Lamloumi, Electrochemical properties of the $CaNi_{5-x}Mn_x$ electrodes synthesized by mechanical alloying, Int. J. Energy Res. 44 (2020) 10112-10125.

[8] Y. Dabaki, C. Khaldi, O. ElKedim, N. Fenineche, J. Lamloumi, Structural, morphological, and electrochemical properties of AB5 hydrogen storage alloy by mechanical alloying, Environ. Prog. Sustain. 41 (2022) e13739.

[9] S.H. Choi, J. Kim, Y.S. Yoon, A TEM study of cycled nano-crystalline HT-$LiCoO_2$ cathodes for rechargeable lithium batteries, J. Power Sources. 135 (2004) 286-290.

[10] A. Bhardwaj, H. Bae, I.-H. Kim, L. Mathur, J.-Y. Park, S.-J. Song, High capacity, rate-capability, and power delivery at high-temperature by an oxygen-deficient perovskite oxide as proton insertion anodes for energy storage devices, J. Electrochem. Soc. 168 (2021) 070540.

[11] Y. Zhang, Y. Ji, W. Zhang, F. Hu, Y. Qi, D. Zhao, Electrochemical hydrogen storage behaviors of as-milled Mg-Ce-Ni-Al-based alloys applied to Ni-MH battery, Appl. Surf. Sci. 494 (2019) 170-178.

[12] R. Monsef, M. Salavati-Niasari, M. Masjedi-Arani, Hydrothermal synthesis of spinel-perovskite Li–Mn–Fe–Si nanocomposites for electrochemical hydrogen storage, Inorg. Chem. 61 (2022) 6750-6763.

[13] L. Ouyang, J. Huang, H. Wang, J. Liu, M. Zhu, Progress of hydrogen storage alloys for Ni-MH rechargeable power batteries in electric vehicles: A review, Mater. Chem. Phys. 200 (2017) 164-178.

[14] W.H. Zhu, Y. Zhu, B.J. Tatarchuk, Self-discharge characteristics and performance degradation of Ni-MH batteries for storage applications, Int. J. Hydrogen Energy. 39 (2014) 19789-19798.

[15] Y.-h. Zhang, X. Wei, J.-l. Gao, F. Hu, Y. Qi, D.-l. Zhao, Electrochemical hydrogen storage behaviors of as-milled Mg–Ti–Ni–Co–Al-based alloys applied to Ni-MH battery, Electrochim. Acta. 342 (2020) 136123.

[16] A.A. Marins, L.M. Boasquevisque, E.J. Muri, M.B. Freitas, Environmentally friendly recycling of spent Ni–MH battery anodes and electrochemical characterization of nickel and rare earth oxides obtained by sol–gel synthesis, Mater. Chem. Phys. 280 (2022) 125821.

[17] H. Chen, L. Zhou, Z. Fang, S. Wang, T. Yang, L. Zhu, X. Hou, H. Wang, Z.L. Wang, Piezoelectric nanogenerator based on in situ growth all-inorganic CsPbBr3 perovskite nanocrystals in PVDF fibers with long-term stability, Adv. Funct. Mater. 31 (2021) 2011073.

[18] T. Yang, Y.-p. Zheng, K.-C. Chou, X.-m. Hou, Tunable fabrication of single-crystalline CsPbI3 nanobelts and their application as photodetectors, Int. J. Miner. 28 (2021) 1030-1037.

[19] F. He, M. Liang, W. Wang, R. Ran, G. Yang, W. Zhou, Z. Shao, High-performance proton-conducting fuel cell with b-site-deficient perovskites for all cell components, Energy & Fuels. 34 (2020) 11464-11471.

[20] Z.N. Garba, W. Zhou, M. Zhang, Z. Yuan, A review on the preparation, characterization and potential application of perovskites as adsorbents for wastewater treatment, Chemosphere. 244 (2020) 125474.

[21] M. Tliha, S. Boussami, H. Mathlouthi, J. Lamloumi, A. Percheron-Guégan, Kinetic behaviour of low-Co AB5-type metal hydride electrodes, Mater. Sci. Eng. B. 175 (2010) 60-64.

[22] W. Zayani, M. Dymek, H. Bala, Comparison of corrosion kinetics of metallic-and ionic materials for negative composite electrodes of NiMH type battery, Ochrona przed Korozją. 4 (2021) 100-105.

[23] W. Zayani, C. Khaldi, J. Lamloumi, Galvanostatic and EIS studies of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ metal hydride anode during cycling, in: 2022 13th International Renewable Energy Congress (IREC), IEEE. 2022, pp. 1-5.

[24] M. Tliha, C. Khaldi, H. Mathlouthi, J. Lamloumi, A. Percheron-Guégan, Electrochemical investigation of the iron-containing and no iron-containing AB_5-type negative electrodes, J. Alloys Compd. 440 (2007) 323-327.

[25] S. Boussami, C. Khaldi, J. Lamloumi, H. Mathlouthi, H. Takenouti, Electrochemical study of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ as negative electrode in alkaline secondary batteries, Electrochim. Acta. 69 (2012) 203-208.

[26] X. Tian, G. Yun, H. Wang, T. Shang, Z. Yao, W. Wei, X. Liang, Preparation and electrochemical properties of La–Mg–Ni-based $La_{0.75}Mg_{0.25}Ni_{3.3}Co_{0.5}$ multiphase hydrogen storage alloy as negative material of Ni/MH battery, Int. J. Hydrogen Energy. 39 (2014) 8474-8481.

[27] A. Kaabi, M. Tliha, A. Dhahri, C. Khaldi, J. Lamloumi, Study of electrochemical performances of perovskite-type oxide $LaGaO_3$ for application as a novel anode material for Ni-MH secondary batteries, Ceram. Int. 42 (2016) 11682-11686.

[28] G. Deng, Y. Chen, M. Tao, C. Wu, X. Shen, H. Yang, Electrochemical properties of $La_{1-x}Sr_xFeO_3$ (x= 0.2, 0.4) as negative electrode of Ni–MH batteries, Electrochim. Acta. 54 (2009) 3910-3914.

[29] G. Deng, Y. Chen, M. Tao, C. Wu, X. Shen, H. Yang, M. Liu, Preparation and electrochemical properties of $La_{0.4}Sr_{0.6}FeO_3$ as negative electrode of Ni/MH batteries, Int. J. Hydrogen Energy. 34 (2009) 5568-5573.

[30] Q. Lin, X. Yang, J. Lin, Z. Guo, Y. He, The structure and magnetic properties of magnesium-substituted $LaFeO_3$ perovskite negative electrode material by citrate sol-gel, Int. J. Hydrogen Energy. 43 (2018) 12720-12729.

[31] Q. Wang, G. Deng, Z. Chen, Y. Chen, N. Cheng, Electrochemical hydrogen property improved in nano-structured perovskite oxide $LaFeO_3$ for Ni/MH battery, J. Appl. Phys. 113 (2013) 053305.

[32] Z.-t. Dong, Y. Li, K.-l. Ren, S.-q. Yang, Y.-m. Zhao, Y.-j. Yuan, L. Zhang, S.-m. Han, Enhanced electrochemical properties of $LaFeO_3$ with Ni modification for MH–Ni batteries, Int. J. Miner. 25 (2018) 1201-1207.

[33] G. Deng, Y. Chen, M. Tao, C. Wu, X. Shen, H. Yang, M. Liu, Study of the electrochemical hydrogen storage properties of the proton-conductive perovskite-type oxide $LaCrO_3$ as negative electrode for Ni/MH batteries, Electrochim. Acta. 55 (2010) 884-886.

[34] C. Rangel, C. Soares, R. Silva, M. Carvalho, M. Jorge, A. Gomes, M. Pereira, High surface area $LaNiO_3$ electrodes for oxygen electrocatalysis in alkaline media, in: 61st Annual Meeting of the International Society of Electrochemistry. 2010.

[35] A. Abbasi, S. Sarker, R.H. Chiang, Big data research in information systems: Toward an inclusive research agenda, J. Assoc. Inf. Syst. 17 (2016) 3.

[36] J. Bian, R. Su, Y. Yao, J. Wang, J. Zhou, F. Li, Z.L. Wang, C. Sun, Mg doped perovskite LaNiO3 nanofibers as an efficient bifunctional catalyst for rechargeable zinc–air batteries, ACS Appl. Energy Mater. 2 (2019) 923-931.

[37] C. Gong, L. Zhao, S. Li, H. Wang, Y. Gong, R. Wang, B. He, Atomic layered deposition iron oxide on perovskite LaNiO3 as an efficient and robust bi-functional catalyst for lithium oxygen batteries, Electrochim. Acta. 281 (2018) 338-347.

[38] Q. Xu, X. Han, F. Ding, L. Zhang, L. Sang, X. Liu, Q. Xu, A highly efficient electrocatalyst of perovskite LaNiO3 for nonaqueous Li–O_2 batteries with superior cycle stability, J. Alloys Compd. 664 (2016) 750-755.

[39] J. Henao, O. Sotelo, M. Casales-Diaz, L. Martinez-Gomez, Hydrogen storage in a rare-earth perovskite-type oxide $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ for battery applications, Rare Met. 37 (2018) 1003-1013.

[40] C. Campos, Solid state synthesis and characterization of NiTe nanocrystals, J. Nano Res. 2014, pp. 35-39.

[41] J. Henao, L. Martinez-Gomez, on rare-earth perovskite-type negative electrodes in nickel–hydride (Ni/H) secondary batteries, Mater. Renew. Sustain. Energy. 6 (2017) 1-14.

[42] L. Forny, I. Pezron, K. Saleh, P. Guigon, L. Komunjer, Storing water in powder form by self-assembling hydrophobic silica nanoparticles, Powder Technol. 171 (2007) 15-24.

[43] J. Shim, K. Lopez, H.-J. Sun, G. Park, J.-C. An, S. Eom, S. Shimpalee, J. Weidner, Preparation and characterization of electrospun LaCoO 3 fibers for oxygen reduction and evolution in rechargeable Zn–air batteries, J. Appl. Electrochem. 45 (2015) 1005-1012.

[44] Y. Dabaki, C. Khaldi, O. ElKedim, N. Fenineche, J. Lamloumi, Phase structure and electrochemical characteristics of CaNi4. 7Mn0. 3 hydrogen storage alloy by mechanical alloying, J. Solid State Electrochem. 26 (2022) 457-468.

[45] Y. Dabaki, C. Khaldi, N. Fenineche, O. ElKedim, M. Tliha, J. Lamloumi, Electrochemical studies on the Ca-based hydrogen storage alloy for different milling times, Met. Mater. Int. 27 (2021) 1005-1024.

[46] I. Karaoud, Y. Dabaki, C. Khaldi, O. ElKedim, N. Fenineche, J. Lamloumi, Electrochemical properties of the $CaNi_{4.8}M_{0.2}$ (M=Mg, Zn and Mn) mechanical milling alloys used as anode materials in nickel-metal hydride batteries, Environ. Prog. Sustain. (2023) e14118.
[47] M. Tliha, C. Khaldi, S. Boussami, N. Fenineche, O. El-Kedim, H. Mathlouthi, J. Lamloumi, Kinetic and thermodynamic studies of hydrogen storage alloys as negative electrode materials for Ni/MH batteries: a review, J. Solid State Electrochem. 18 (2014) 577-593.
[48] K. Ren, Z. Duan, Y. Li, L. Zhang, S. Han, Electrochemical Charge and Discharge Performance of Perovskite-Type Oxide $La_{1-x}Na_xFeO_3$ (x= 0–0.8) in Alkaline Solution, J. Electrochem. Soc. 168 (2021) 043501.
[49] A. Khedimallah, Y. Dabaki, A. Kaabi, C. Khaldi, M. Molière, O. ElKedim, N. Fenineche, J. Lamloumi, Electrochemical study of the $LaFe_{0.8}Ni_{0.2}O_3$ perovskite-type oxide used as anode in nickel-metal hydride batteries, Ceram. Int. 48 (2022) 31157-31171.
[50] W. Zayani, S. Azizi, K.S. El-Nasser, I. Othman Ali, M. Molière, N. Fenineche, H. Mathlouthi, J. Lamloumi, Electrochemical behavior of a spinel zinc ferrite alloy obtained by a simple sol-gel route for Ni-MH battery applications, Int. J. Energy Res. 45 (2021) 5235-5247.
[51] A. Kaabi, M. Tliha, A. Dhahri, C. Khaldi, N. Fenineche, O. Elkedim, J. Lamlouli, Effect of temperature on behavior of perovskite-type oxide $LaGaO_3$ used as a novel anode material for Ni-MH secondary batteries, Int. J. Energy Res. 42 (2018) 2953-2960.
[52] W. Zayani, S. Azizi, K.S. El-Nasser, Y.B. Belgacem, I.O. Ali, N. Fenineche, H. Mathlouthi, New nanoparticles of (Sm, Zn)-codoped spinel ferrite as negative electrode in Ni/MH batteries with long-term and enhanced electrochemical performance, Int. J. Hydrogen Energy. 44 (2019) 11303-11310.
[53] H. Mathlouthi, C. Khaldi, M.B. Moussa, J. Lamloumi, A. Percheron-Guégan, Electrochemical study of mono-substituted and poly-substituted intermetallic hydrides, J. Alloys Compd. 375 (2004) 297-304.
[54] M. Song, Y. Chen, M. Tao, C. Wu, D. Zhu, H. Yang, Some factors affecting the electrochemical performances of $LaCrO_3$ as negative electrodes for Ni/MH batteries, Electrochim. Acta. 55 (2010) 3103-3108.
[55] M. Tliha, A. Kaabi, C. Khaldi, A. Dhahri, N. Fenineche, O. ElKedim, J. Lamloumi, Electrochemical study of $LaGaO_3$ as novel electrode material of hydrogen battery (Ni/MH), Environ. Prog. Sustain. 42 (2023) e13930.
[56] P. Liu, J.Y. Hu, Q.R. Yao, J.Q. Deng, Z.M. Wang, H.Y. Zhou, Structure and Electrochemical Properties of $La_{1-x}Ba_xCoO_3$ Powders as Negative Electrode Materials for Ni/MH Batteries, in: Materials Science Forum, Trans Tech Publ. 2015, pp. 113-117.
[57] K. Ren, L. Zhang, J. Miao, J. Zhao, S. Yang, Y. Fu, Y. Li, S. Han, Boosting the high-temperature discharge performance of nickel-hydrogen batteries based on perovskite oxide Co-coated LaFeO3 as proton insertion anode, Int. J. Hydrogen Energy, 47 (2022) 14961-14970.
[58] G. Deng, Y. Chen, M. Tao, C. Wu, X. Shen, H. Yang, M. Liu, Electrochemical properties and hydrogen storage mechanism of perovskite-type oxide LaFeO3 as a negative electrode for Ni/MH batteries, Electrochim. Acta, 55 (2010) 1120-1124.
[59] S. Azizi, M. Salah, H. Nefzi, C. Khaldi, F. Sediri, E. Dhahri, J. Lamloumi, Structure, volumetric adsorption method and electrochemical hydrogen storage properties of vanadium oxide nanotubes VOx-NTs, J. Alloys Compd., 648 (2015) 244-252.
[60] M. Tliha, C. Khaldi, J. Lamloumi, AC Impedance Behavior of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.6}Fe_{0.15}$ Hydrogen-Storage Alloy: Effect of Surface Area, J. Mater. Eng. Perform., 25 (2016) 1578-1585.