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Electrochemical Performance of La_2O_3 /TiO_2 and Effects of Ball Milling

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La_2O_3 powders were mixed with TiO_2 powders to obtain a better alloy that can be used as energy storage. The influence of La_2O_3 with TiO_2 was studied by electrochemical noise (EN); powders were made by ball milling, sintered and then characterized. The experimental results showed that the samples generated had a good response under NaOH; using EN technique in sintered samples and green samples (without sintering process). Solution samples had a disturbance response when adding Na_2SO_4. These results were conducted by using potentiodynamic polarization curves. Behaviors in potentiodynamic polarization curves showed a greater disturbance since lanthanum is a reactive material, but satisfactory results were obtained in complete curves. The X-ray diffraction (XRD) and (TEM) images presented an interesting structure and morphology to be used in order to clarify whether exist a pattern of behavior in samples made by ball milling, sintering process and milling time. The electrochemical studies and images obtained by TEM were also investigated. As a work electrode material, La_2O_3 doped with TiO_2 had a good response at corrosion environment. The current results aimed at improving and designing a better electrode by researching degradation and their changes in microstructure.

Keywords: Mechanical Alloying, Electrochemical Noise, Morphology, Energy Storage Materials, Characterization.

1. INTRODUCTION

New combination of materials has recently become of greatest importance to generate options in order to better understand the charge, discharge and behavior of materials related to energy storage. In this regard, secondary batteries with their electrochemical performances have been developed as high energy density, high power density, high open circuit voltage, low cost and environment-friendliness [1]; previous knowledge then allow to take the advantage of employing ball milling from other research works related to corrosion, and thus design an electrode with improved behavior pattern.

Development of Ni–Zn battery is restricted because of its defects such as dissolution of active material, dendrite growth and shape change of zinc electrode [1]. Dendrite growth was observed in mechanical alloying made by ball milling with other materials [2], but La alloying with TiO_2 was not envisaged in this research. To improve the performance of materials used as a battery, many efforts have been undertaken. Therefore, ball milling is considered in this research as a good tool to obtain new electrodes and controlling milling time, sintering time and understanding the pattern of samples.

Since the second half of the twentieth century, metal matrix composites (MMCs) have been considered as one of the important materials. MMCs have made their ways into various applications in aerospace, electronic packaging, and automotive industries [3].

La_2O_3 is a highly efficient lithium ion conductor coated with $LiCoO_2$; particles possess high discharge capacities and excellent cycle stability [4]. In this study, La_2O_3 doped TiO_2 as a work electrode was prepared by ball milling at different milling times. The effects of these samples on electrochemical performance were investigated. The first electrochemical technique test was EN since their process protects samples, unlike other techniques as impedance. The good response of the results prompted the next step to test other techniques, in this case potentiodynamic polarization curves. Such a technique brings up the opportunity to analyze the morphology of samples by TEM, having in mind to reduce or increase milling time; but attending the possibility of contamination. Images were studied to understand samples behavior to reduce time and resources in laboratory and find out a better electrode to be used as a material storage. In some cases, the high energy milling appears to effectively break up large aggregates into smaller particles. The milled $LiMnBO_3$ powders exhibit a huge improvement in charge-discharge capacities compared to the milled counterparts [5]. Actually, the ball milling and its influence on the synthesis temperature, the morphology and electrochemical performance of $Li_4Ti_5O_{12}$ were investigated for several reasons [6], one of them is that the high-energy ball milling was used to design a supercapacitor electrode with nanoscale [7]. Nanoscale is important in this investigation because it allows creating a better option for the electrode.

Mechanical milling process was considered as an important route for the fabrication of composites, since the dispersion of the reinforcement is carried out in solid state, unlike casting routes [8]. In this work the variations in sintering process and green samples were analyzed. Likewise the effects of sintering, milling time, and electrochemical response were investigated on the proposed electrode.

Other research works have reported that high-energy ball milling gave rise to a better nanocrystalline structure, extended solubility, uniformly distributed fine particles, and homogenous microstructure and corrosion resistance [9]; while others concluded that high-energy ball milling process is a simple, low cost and promising approach [10].

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Electrodes by Ball Milling

Commercial powders used from Sigma Aldrich: Lanthanum oxide (99.0% purity), Titanium Oxide (99.5% purity) was used. Hardened stainless steel balls with 13 mm(Ø) balls were loaded into SPEX 8000M connected to a hardened steel container as milling media and an Ar atmosphere. Milling intervals were 0, 2 and 4h using alternate cycles of 30 min milling and 30 min resting. The milling ball was kept 5 to 1 for all experimental tests. The density pycnometer of powders of 0, 2 and 4h are shown in Table 1. The best performance was observed in 2h of milling time. Figure 1 shows the X-ray patterns at 2h and 4h where is clearly observed that 4h presents the best density; regarding the samples microstructure, however, a better stability was found at 2h. The diffraction profiles were measured by a Philips X'pert powder diffractometer using a Cu cathode (= 0.15406 nm). Powders was analyzed by pycnometer of Helium, the gas used was Nitrogen. The samples testing to obtain density, was measured by (gr. /c.c.) gram by centimeter cube. Density was calculated by d= m/v; where d= density, m = mass, v =volume in S.I (International System of Units).

$$d = \frac{m}{v} \qquad (1)$$

Table 1. Milling time and density values of powders of La_2O_3/TiO_2.

Milling Time	Density	Volume
0 h	4.7800 ± 0.175 g/c.c	0.4778 c.c
2h	5.1658 ± 0.365 g/c.c	0.4667 c.c
4 h	5.6616 ± 0.434 g/c.c	0.4382 c.c

In the current study, contamination and process of ball milling was considered to be an important standpoint. In this context, the advantage of porosity was really helpful to improve the mixture of powders and stop milling time until contamination could be observed. Although several works define ball milling technique as a complicated process, it does confirm the potential contamination from the high-energy ball milling procedure; particle size analysis could also be used to study the microstructural evolution and morphological changes during the milling process [11].

During milling time, it was clearly observed that 2h of milling is sufficient to mix powders, because La_2O_3 was overpowered with more milling time. Increasing milling time at 4h permits mix powders but lost TiO_2 and La_2O_3 was predominant in peaks noted; this was the reason to use as a main material for electrode use at 2h. Increasing milling time at 4h allowed the mixing of powders, however, the loss of TiO_2 and La_2O_3 was predominant during peak times; reason by which was used as the main material for the electrode at 2h. The increase of milling time was not an option in this analysis, because powders tend to loss it in vial steel hardness with one more hour of milling (5h). In this research the step size and step time was 0.0330 and 60 s at 25° C, respectively. X-ray diffraction peak profile analysis was carried out to determine the crystallite size. The granule morphology, granule size distribution, crystallinity and molecular weight have been reported to be significantly modified by ball-milling [12].

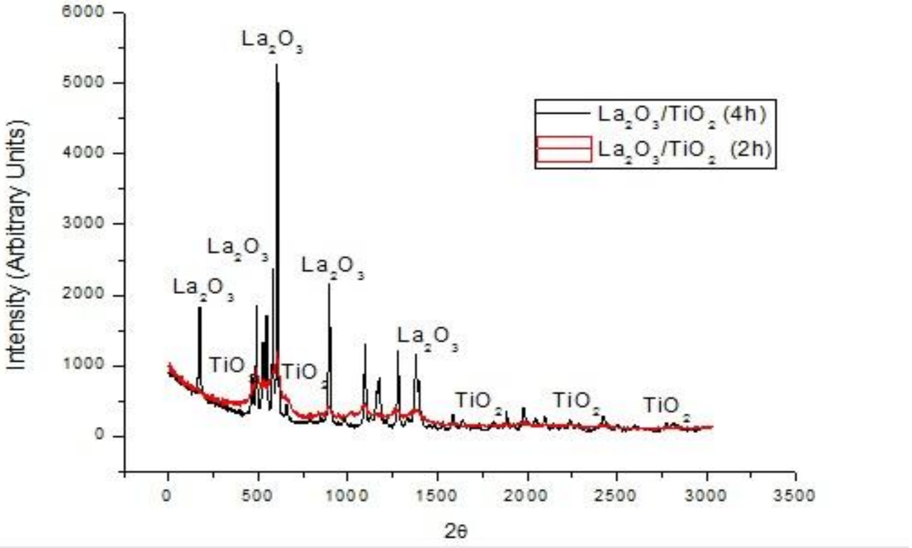

Figure 1. X-Ray diffraction pattern of La_2O_3/ TiO_2 at 2 and 4 h.

2.2 Temperature Treatment

Synthesis of nanomaterials under high temperature has been shown to present difficulties, nevertheless lanthanum oxides has also been recognized as an excellent host for RE (rare-earth) activators [13]. In this study, the milling samples were placed in an electric furnace at 700 °C for 4h. Subsequently, the samples were cooled down by 50°C and then allowed to cool naturally to room temperature. Some studies reported that cathode produced by La_2O_3 cannot be heated up or the temperature could be inadequate for activation [14]. In this analysis, the temperature produced significant changes in color samples. The La_2O_3/TiO_2 binary system have been studied experimentally and calculated by numerous investigators and their results are somewhat inconsistent [15-16-17], some of these reasons of the La behavior were due to the electronic configuration and size of the lanthanide atoms [18]. In the current study, the changing color in samples and loss of powder during milling were the main reasons for not increasing milling time.

2.3 Electrochemical Analysis

Electrochemical noise (EN) measurements are gradually becoming accepted for the study of corrosion processes, although much remains to be done in developing a complete understanding of the interpretation of EN. Furthermore, there is considerable evidence that many EN measurements are contaminated by extra noise and measurement artifacts of various sorts [19-20]. In the current experimental work, disturbance o extra noise could only be observed with potentiodynamic polarization curves.

In order to understand the sample behavior and before using it as a storage material, EN tests of La_2O_3/ TiO_2 samples were performed. Samples were immersed in NaOH solution for half an hour for stabilization and the open circuit potential was measured during this period with a multimeter; the OCP samples were -161 and -226 mV vs SCE for 2h to 4h milling of green samples (without sintering process) in an average. The reading points were 1024. The sintering samples (sintered in electric furnace) were -400 and -405 mV vs SCE for 2h to 4h for milling in average. All tests were performed at room temperature (25° C). Gill AC -ACM Instruments equipment was used. In the case of Na_2SO_4 solution, the OCP were -98.67 and -356.61 mV SCE for green samples. For the sintered samples, the disturbing results oriented the experiment not to test it using potentiodynamic polarization curves with Na_2SO_4 solution. The average results were -47.36 and -124.8 mV.

3. RESULTS AND DISCUSSION

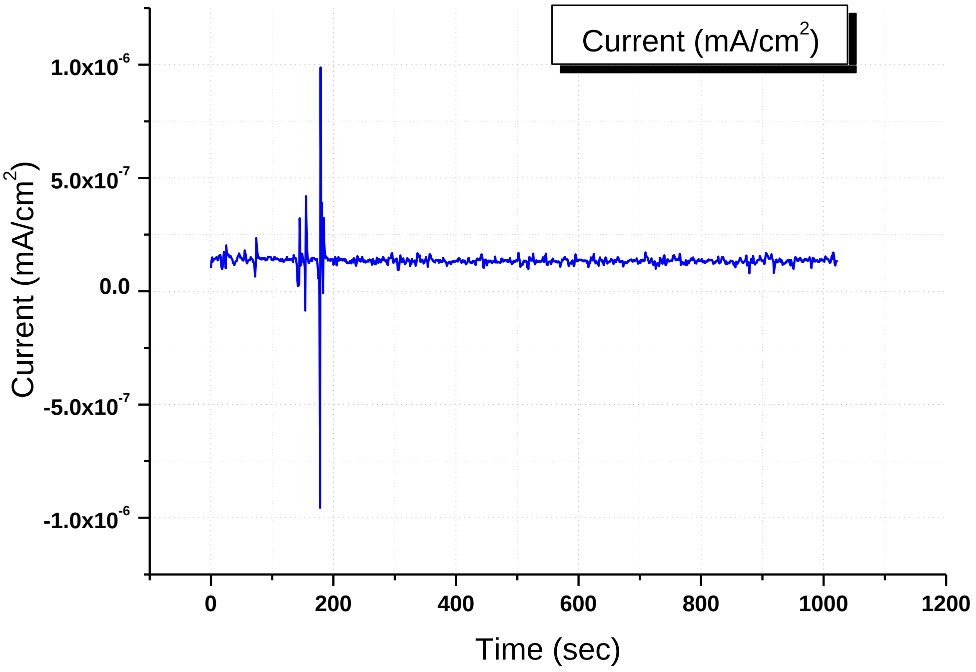

Figure 2a. Electrochemical noise result of $La_2O_{3/}$ $TiO_{2,}$ green sample at 4h in NaOH solution.

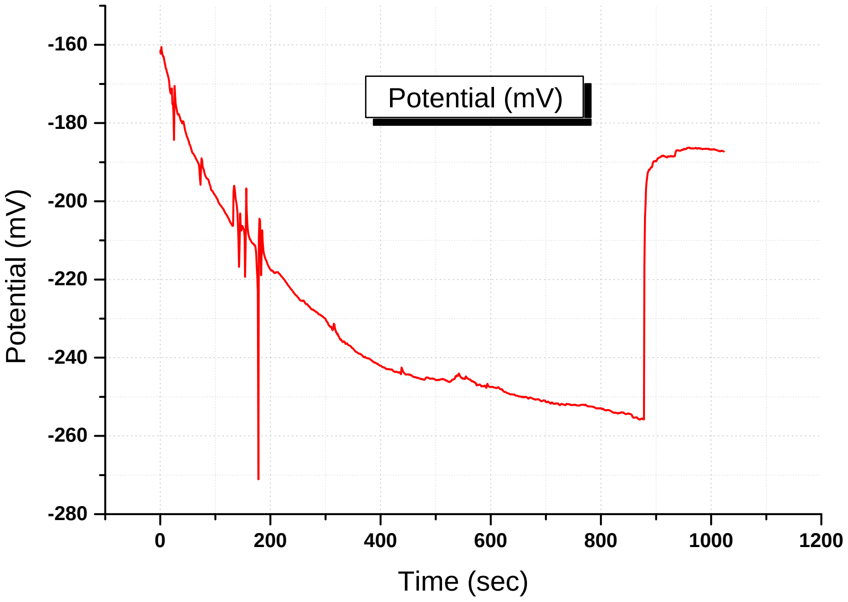

Figure 2b. Potential information vs time of La_2O_3/ TiO_2 samples.

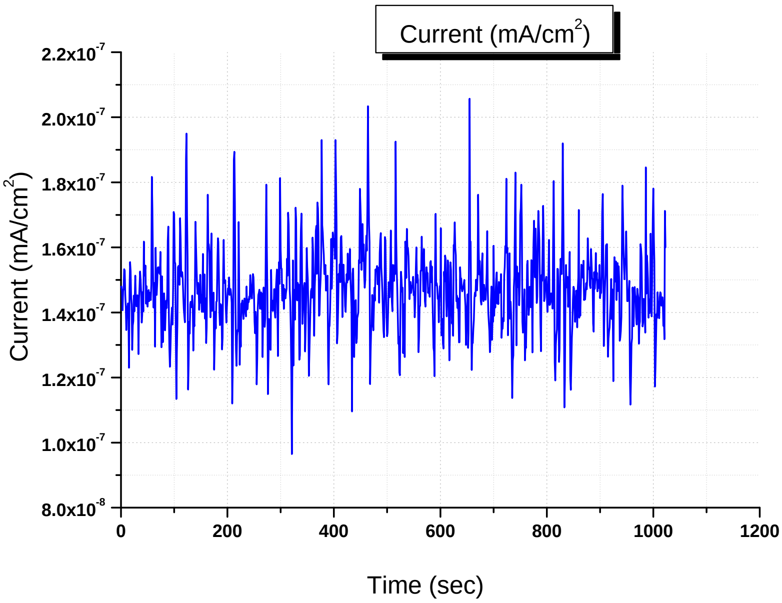

Figure 3a. Current vs time of EN of La_2O_3/ TiO_2 , sintered sample at 4h in NaOH solution.

Figures 2a, 2b, 3a and 3b show the plots obtained experimentally by EN. *In these plots, i*t was observed that as the average values of green samples presented 1.518E-07 in current (mA/cm²), the sintered samples had a difference because of the temperature applied. After sintering, the values of green samples were 1.555E-07 in current (mA/cm²).

In some investigations, super electrochemical performance was found when using EIS (Electrochemical Impedance Spectroscopy) fitting results *and t*he exchange current density at 800 °C in La from an aqueous solution; whilst La_2O_3 alloys were used as a cathode elsewhere [21-22]. In this study, EIS was not considered because the potentiodynamic polarization curves technique was applied.

Figure 1 shows XRD plots of the La_2O_3 composite during time milling at 2h and 4h. Evident increase in the magnitude of the relative peaks corresponding to 4h (black color) phase Lanthanum was observed with less stability because of the loss of TiO_2 powders, while density was higher than 2h.

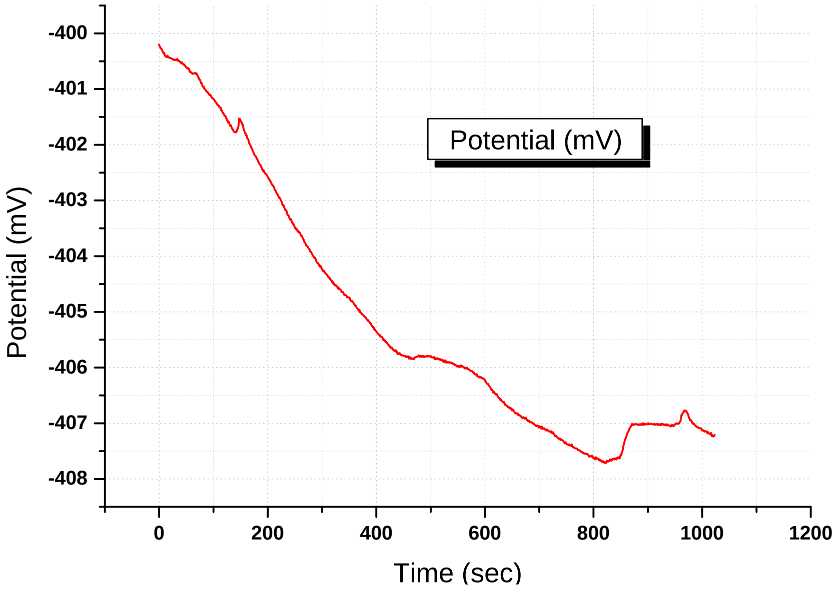

Figure 3b. Relationship of EN of La_2O_3/ TiO_2 , sintered sample at 4h in NaOH solution.

Studies related to Lanthanum have shown that the corrosion noise potential oscillated between –0.93 and –0.98 V for samples with protective behavior of La (III); in some cases no significant differences appeared in the behavior of the metal coated [23]. Some other investigations, as in this study, did not find any differences in metal coated with others materials as Ti, Al, V mixed by ball milling [2]; hence green samples and sintered samples were considered as a good corrosion response. In this case using La and Ti O_2 was not applicable.

Regarding the electrochemical polarization using Lanthanum, different times between 20 and 30 min and potentials in the range of -1.5 V to -3.5 V in cathodic and +1.0 V to +2.8 V in anodic direction at 550 °C have been reported [24]. Lanthanum structure and its good electrochemistry properties is bond with other materials as Nb and remain high electrochemical activities [25-26]. In this research TiO_2 was considered to be the best option to increase the good electrochemical behavior of Lanthanum. Figure 5a) shows a TEM micrograph with 2µm in average of particle size; Figure 5b) shows the micrograph obtained by optical microscopy with 50µm, here it can be seen that samples tend to split up; this situation may be the cause to obtain a good electrochemical response in polarization curves.

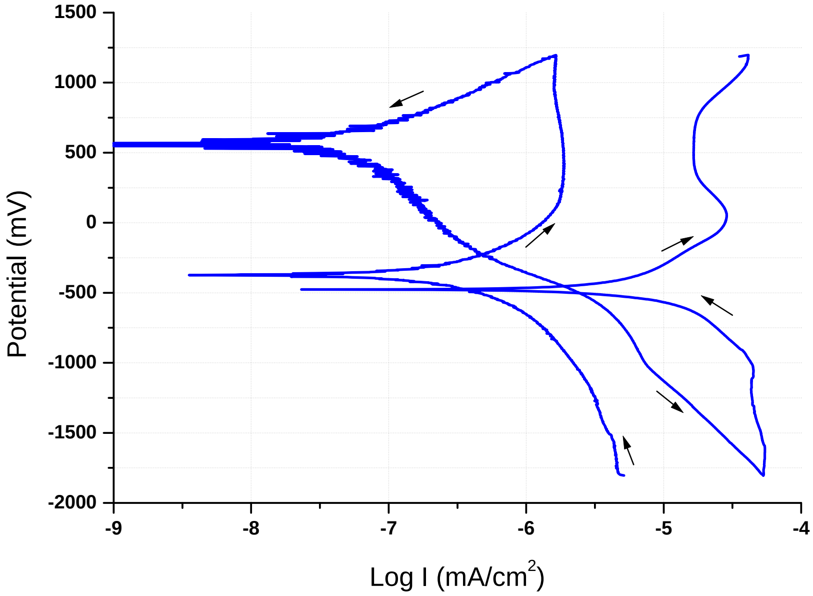

Figure 4. Potentiodynamic polarization curves La_2O_3/TiO_2 sintered samples.

Table 2. Electrochemical performance of La_2O_3/TiO_2 sintered samples.

Milling Time Sintered Samples	**R_n (ohm.cm^2)**	**E_{corr} (V)**	**I_{corr}**
2h	1.469E+07	-356.51	8.17E-07
4 h	1.795E+08	-98.677	9.747E-08

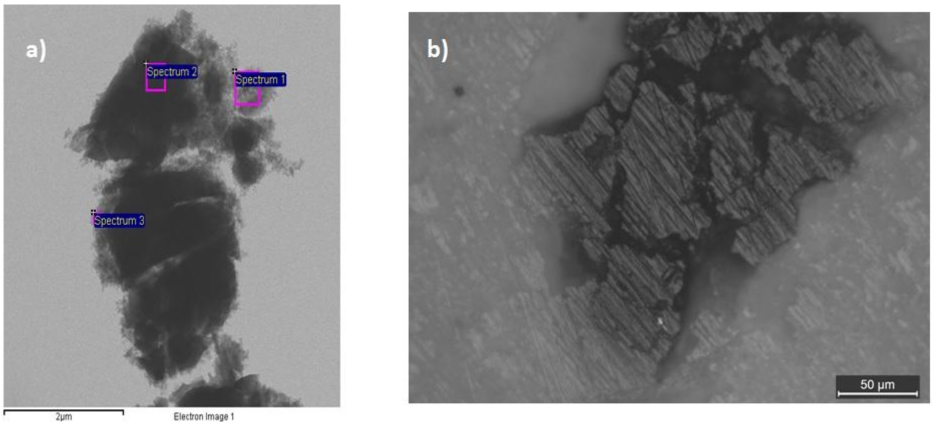

Figure 5. a) TEM of La_2O_3/ TiO_2 green samples at 2h of milling time and b) micrograph obtained by optical microscopy of La_2O_3/ TiO_2.

A separate structure was observed for the milling time at 2h in the La_2O_3/ TiO_2 green samples, where the reaction in physical color was appreciated as white color. Figure 4 illustrates the performance of potentiodynamic polarization curves in La_2O_3/ TiO_2 under Na_2SO_4 in sintered samples. Likewise it is observed that temperature tend to lose the stability of the samples in some regions, this corresponding to the studies obtained in the X-Ray results. Table 2 shows the electrochemical Tafel slopes results of La_2O_3/TiO_2 sintered samples, observing the E_{corr} between 2h and 4h. Similarly, the best time under electrochemical test was attained at 2h.

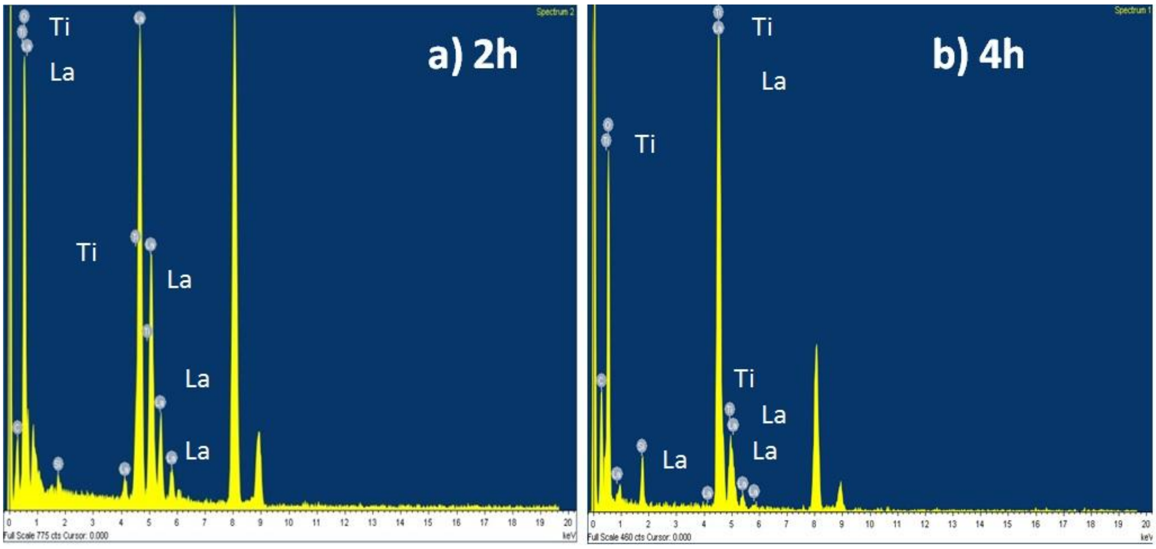

Figure 6. a) EDEX of La_2O_3/TiO_2 sintered samples at 2h and b) Composition of samples at 4h.

Figures 6a) and 6b) explain the composition of samples at 2h and 4h; at 4h, La is distributed in the similar position as a result of the XRD. Figures 7a), b), c) and d) show the average particle size.

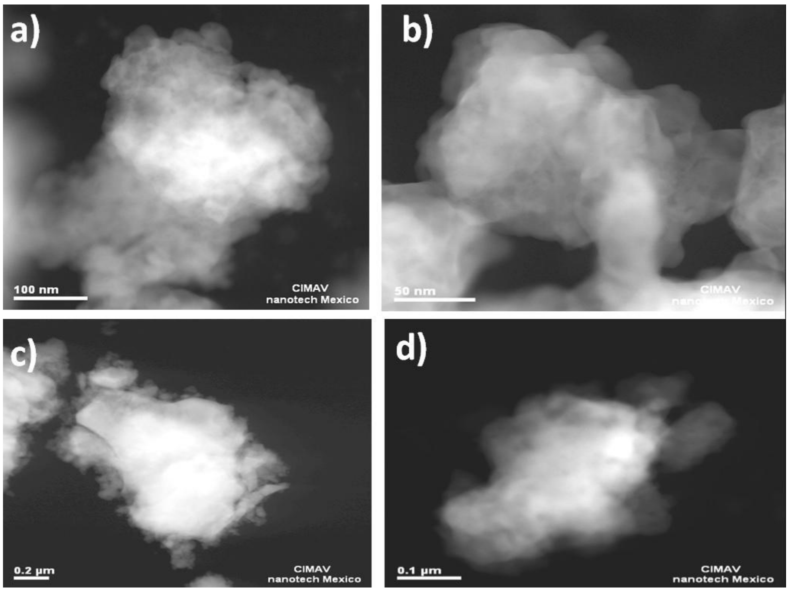

Figure 7. a) Morphologies of La_2O_3/TiO_2 particles at 100nm; b) Increasing milling time 5nm; c) Dimension of particles 0.2µm; d) Minimal size average found (0.1µm).

In order to determine La(III), a highly sensitive electrochemical sensor was successfully developed and tested by electrochemical techniques [27-28], and one of the most important types of potentiometric sensors is carbon paste electrode [29-30]. Figures 5a) and 5b) show the micrographs obtained by TEM and optical microscopy. As a green product, samples show spaces in between; this can be understood as porosity, taken as a reference for the results obtained by electrochemical performance.

The morphologies and dimensions of these particles were very similar with a crystallite size, which coincided with the XRD results elsewhere [31-32]. *Throughout the investigations,* high purity La_2O_3, TiO_2 and Nb_2O_5 powders (99.99%) were used and mixed in the stoichiometric ratio of $20La_2O_3$-(80-x) TiO_2-$x$$Nb_2O_5$ (x=0-80, Δx =5). *T*he mixture was compacted and then sintered at 1100°C for 10 hours [33-34]. This type of experiments allowed for a better understanding on the behavior of La_2O_3/TiO_2 under different temperatures and milling times.

4. CONCLUSIONS

- Ball milling as a tool with materials that contain La_2O_3 require in depth analysis. The increase of milling time in other materials can be an acceptable approach to obtain better results and good mixture or alloying.
- Lanthanum composite needs a sintered process and a different kind of material to improve their corrosion resistant. Behavior of Lanthanum was not possible to observe by the images obtained in this investigation.
- Concerning the energy storage, the research of new materials becomes fundamental to improve the electrochemical performance of Lanthanum. The results obtained by potentiodynamic polarization curves, permitted not to consider cyclic voltammetry test with this kind of electrodes.
- La_2O_3 doped with TiO_2 nanocrystalline powder was prepared at low hours of milling time, having in mind to control the reaction; this control cannot be controlled for more than 5 hours. The use of TiO_2 did not work well to create a good electrode to protect Lanthanum.
- The time milling could be increased using Lanthanum but without using TiO_2.

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