



Properties and Characteristic of Perovskite Type $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$

A. Guemache^{1*}, A. Bouchelaghem², M. Drif², F. Kahoul³, L. Hamzioui³

¹ Université de M'Sila, Département d'hydraulique, Faculté de Technologie, M'Sila 28000 Algérie

² Université de M'Sila, Département d'Électronique, Faculté de Technologie, M'Sila 28000 Algérie

³ Université de M'Sila, Département Socle Commun ST, Faculté de Technologie, M'Sila 28000 Algérie

Corresponding Author Email: abderezak.guemache@univ-msila.dz

<https://doi.org/10.14447/jnmes.v25i2.a09>

ABSTRACT

Received: July 21, 2021

Accepted: October 15, 2021

Keywords:

Perovskite, co precipitation, Thermal analysis, Electrochemical comporment

$\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0, 0.1, 0.2$) nanoparticles were synthesized by the co-precipitation method. The structural analysis reveals the presence of Octahedral coordination of MnO_4 . Fourier transform infrared spectroscopy (FTIR) spectra of MnO_4 show the occurrence of O-Mn-O vibrational mode at around 590 cm^{-1} . The XRD indicates that the samples are Rhombohedral lattice. The differential and thermo gravimetric analysis, curve obtained from the composition $x=0.1$, it has distinct pure phase at 600°C . The study of electrochemical behavior was carried out by cyclic Voltammetry (CV) and impedance spectroscopy (EIS). Show that the apparent electrochemical activity improves by increasing the strontium concentration. This is due to the particle size effect of strontium.

1. INTRODUCTION

Mixed conductor oxides find interesting applications in a variety of technological fields in electrochemistry and catalysis. Used in a dense membrane, they are of growing interest in the catalytic conversion of natural gas to synthetic gas through improved process efficiency and lower costs than current technologies.

The latter has strong catalytic activities in various fields of application and high thermal stability and are considered as potential catalysts in substitution for noble metals such as platinum and palladium [1,4].

These include the work of Balachandran et al. [5,6] which demonstrated the possibility by using dense tubes, made from a mixed conductive oxide, to achieve partial oxidation of methane.

Numerous studies have shown that powder size, morphology, texture and non-stoichiometry play a very important role in the intrinsic properties of these materials [7-8 -9]. The important activity is attributed to metal oxides in which the metal can have several oxidation states and create large specific surfaces.

The traditional method of so-called dry synthesis offers the advantage of being simple and inexpensive, but requires several treatments at high temperature to achieve homogenization of the product. Despite this, the materials obtained have large grain sizes and small specific surfaces [10].

For these reasons various investigations are currently underway to increase the catalytic efficiency of these materials by varying the nature of the doping at sites A and B of the cationic network and with the development of new methods preparation of these oxides [11, 12, 13].

The elaborations that we have realized apply on the oxides of manganese, calcium and strontium. It consists in determining the optimal conditions for the synthesis of these materials and studying their electrochemical behavior for possible applications as electrode material vis-à-vis the oxygen reduction and release reactions in the middle of alkaline.

2. EXPERIMENTAL

Preparation of CaMnO_3 , partial substitution of calcium with strontium ($\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$) with $x = 0, 0.1, 0.2$, prepared by the method co - precipitation method is considered. For the preparation of the precursors soda hydroxides, the nitrates of the metals of Ca, Mn, Sr are dissolved separately in a volume of 25 ml distilled water then mixed. The soda (pro lab) 14 N is gradually added to the mixture in order to co-precipitate the hydroxides of the three metals.

The basic heterogeneous solution obtained is agitated for one hour. On the other hand, to remove the supernatant, centrifugation (6000T/minute) is used for 20 minutes; the resulting precipitate is then washed 4 times with distilled water and 2 times with ethanol. Removes residual water, and the precipitate is placed in an oven overnight at a temperature of 110°C . The resulting precursor is then ground, calcined for 6 hours in an electric furnace (Pyro) at a temperature of 1000°C .

The resulting phase analysis was performed by recording the X-ray diffract grams of powder using an Xpert Pro (Panalytical) diffract meter using the $\text{CuK}\alpha$ radiation of copper ($\lambda = 1.5418\text{ \AA}$) and infrared spectroscopy.

The behavior of the precursors as a function of temperature was followed by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using a TG 409

PC LUXX nitrogen device. The electrochemical study was conducted using two methods, cyclic voltametry and impedance spectroscopy using a PGZ 301 Volta lab 40. The reference electrode used is Hg/ HgO/ 0.1 M KOH

3. RESULTS AND DISCUSSIONS

3.1 Infrared spectroscopy analysis and X-ray diffraction

The infrared spectra of the x-composition oxides = 0, 0.1 and 0.2 recorded in a frequency range 400-3000 cm^{-1} show an intense peak at 590 cm^{-1} and a relatively small one at about 414 cm^{-1} (Fig 1). Both peaks are characteristic of perovskite oxides and can be attributed respectively to the modes of elongation Mn-O and O-Mn-O torsion [14].

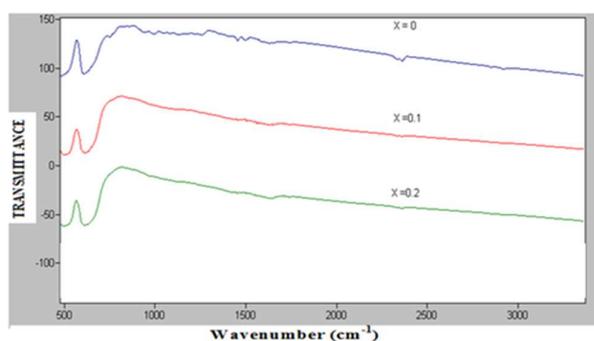


Figure 1. Infrared spectra $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.2$)

In order to further confirm the formation of the perovskite phase, all powder diffracts grams relative to the system. $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.2$) were recorded (Fig 2). It indicates that in all cases that this synthesis method has led to perovskite structure oxide where manganese is in octahedral coordination. The network constants do not vary significantly by substituting calcium by strontium due to the size very close to the cations $r_{\text{Ca}^{2+}} = 1.34 \text{ \AA}$, $r_{\text{Sr}^{2+}} = 1.44 \text{ \AA}$

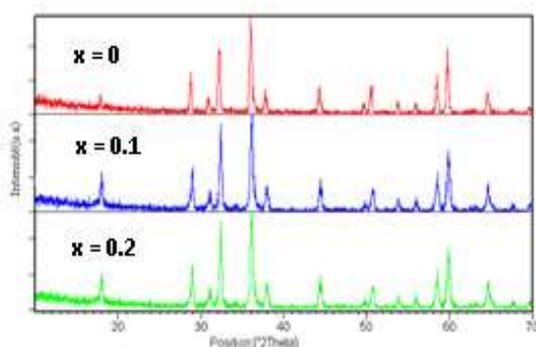


Figure 2 . DRX of $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.2$)

3.2 Thermal analysis

Fig 3 shows a differential and thermo gravimetric thermal analysis, curve obtained from the composition $x = 0.1$. It has three distinct mass losses at temperatures of 25-220, 220-320 and 320-600 $^{\circ}\text{C}$. The ATD curve has a broad exothermic peak at 220-320 $^{\circ}\text{C}$, a narrow endothermic peak at about 620 $^{\circ}\text{C}$.

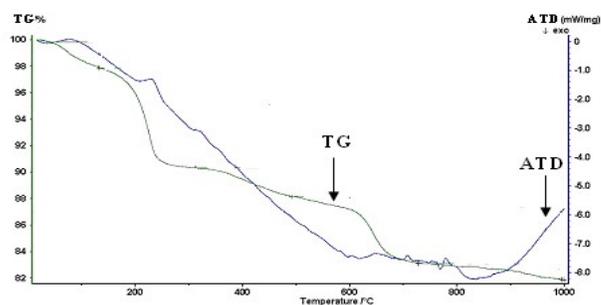


Figure 3. Thermo gravimetric and differential Curve of $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$

The first loss of weight of 25 to 220 $^{\circ}\text{C}$ is accompanied by an endothermic peak attributed to the loss of residual water. The second mass loss accompanied by a large exothermic peak corresponds to the decomposition of nitrates. The third gradual weight loss of 320 to 600 $^{\circ}\text{C}$ associated with a narrow exothermic peak in Approximately 600 $^{\circ}\text{C}$ is the entrance to the oxide training area. From this result, we proceeded to process our samples at temperatures from 600 $^{\circ}\text{C}$ and above until the pure perovskite phase was obtained [15].

3.3 Electrochemical comportment

3.3.1 Cyclic Voltametric

Fig 4 presents the cyclic voltamograms of $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.2$) oxides in the KOH medium (0.1 M) in the air, where the scanning speed is 20 mv/s in the range of potential between -1.5 and +1 V (Hg/HgO). The Voltamograms of the $x = 0, 0.1$ compositions show relatively low anodic and cathodic currents. On the voltamogram for the composition $x = 0.2$, a relatively strong cathodic and anodic peak appears in the potential domains between -1.5 and -1V, 0.5 and 0.75 V respectively.

The slight difference in oxygen surge between the different substitutions is probably due to the small amount of oxygen present in solution after bubbling with nitrogen[16]. It can then be said that it is the composition $x = 0.2$ which apparently combines all the advantage to be the best electrode from the electro activity point of view.

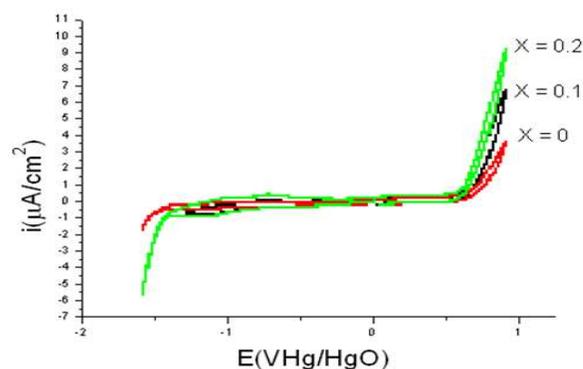


Figure 4 . Voltamogrammes relatifs à l'oxyde $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0, 0.1, 0.2$)

The densities of the currents obtained (Table 1) show that the apparent electro catalytic activity of the doped electrodes is greater than that of the electrode without strontium. Indeed the electrode substituted by 20% in strontium is almost six times higher than that not substituted. They are of the same order of magnitude as those obtained for the systems $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ [17], LaMnO_3 [18] and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [19] at nearby potential values.

This behavior is probably due to the strontium introduced into the oxide, which causes the load transfer to the electrode surface to activate. Similar studies on doped perovskite oxides have shown that the catalytic activity of these compounds in relation to oxygen release is high when the doping level increases [20].

Table 1. Kinetic Parameters for Oxygen reduction and evolution on Oxide Electrodes $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.2$) in KOH (0.1M) à 25°C

Electrodes	$i_c / \text{mA.cm}^{-2}$ E = -1.6V	$i_a / \text{mA.cm}^{-2}$ E = 0.8 V
CaMnO_3	0.6	1.3
$\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$	0.8	2.3
$\text{Ca}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	2.9	5.9

3.3.2 Electrochemical impedance spectroscopy

The Nyquist diagram shown in (Fig 5) is obtained from $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ oxide workflow electrodes ($0 < x < 0.2$), submerged for 20 minutes in a solution of KOH 0.1M in a wide range of frequencies (10^{-5} - 10^{-2} Hz). A linear part of this diagram (right of Warburg) making an angle of 45° to the axis of the real is related to a diffusion process. For both compositions $x = 0$ and 0.1, the diagrams are Super imposable indicating a similarity of the characteristics of these two electrodes

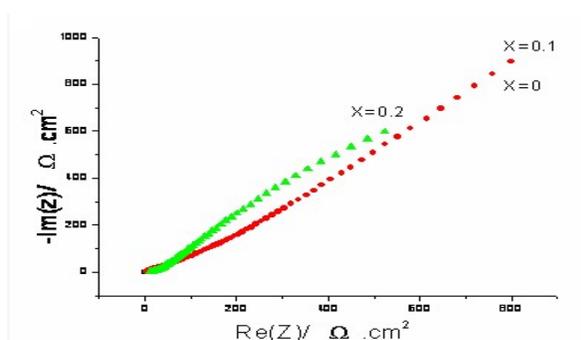


Figure 5. Impedance diagrams of the $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.2$) electrodes in KOH (0.1M).

The magnitudes of the impedance spectroscopy namely the load transfer resistance r_{tc} , the resistance of the Re electrolytes are collected in Table 2. It is noted that the r_{tc} load transfer resistance decreases when the substitution rate increases. This also confirms the electro catalytic character of these oxides which intensifies as the strontium level increases

Table 2 . Variation of the magnitudes of the impedance of the electrodes according to the composition x.

x (Sr rate)	$R_{tc} (\Omega.\text{cm}^2)$	$R_e (\Omega.\text{cm}^2)$
0	37.5	27.2
0.1	37.5	27.2
0.2	13.2	29.2

4. CONCLUSIONS

Analysis by infrared spectroscopy and X-ray diffraction enabled the structure of the oxides prepared by the co-precipitation method to be identified. Thermo gravimetric and differential analysis (ATG/ATD) we have been able to characterize the different transformations that take place during a heating cycle and determine the Calcinations temperature corresponding to the passage from the hydroxide form of the various metals to the oxide form.

On the other hand, the study of electrochemical behaviour on these $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ oxide electrodes characterized by two techniques showed that: the cyclic voltametry allowed to characterize the interface of the electrodes studied in medium KOH 0.1 M. Indeed, the densities of the cathodic and anodic currents obtained are all the greater as the x substitution in the electrode material is high.

The impedance spectroscopy also confirms the advantage of strontium substitution for this system according to the values of the r_{tc} load transfer resistance obtained.

Finally, it can be concluded that the electro-catalytic activity of $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ oxides synthesized by the co-precipitation method is better for the highest strontium-rich composition through the evolution of oxygen in KOH 0.1 M at 25°C. In the range of anodic current densities from 1.3 to 5.9 mA / cm² and a potential of 0.8 V.

REFERENCES

- [1] Seyed AliHosseini,DariushSalari(2013).Journal of industrial and Engineering Chemistry,6,1903-1909.<https://doi.org/10.1016/j.jiec.2013.02.034>
- [2] L.G. Tajuca, J.L.G. Fierro (1989) ,Adv. Catal., 36 -237. [https://doi.org/10.1016/S0360-0564\(08\)60019-X](https://doi.org/10.1016/S0360-0564(08)60019-X)
- [3] L.Simonot, F. Garin, G. Maire(1997) , Appl. Catal., B 11 -167. [https://doi.org/10.1016/S0926-3373\(96\)00046-X](https://doi.org/10.1016/S0926-3373(96)00046-X)
- [4] R.N. Singh, T. Sharma, A. Singh, Anindita, D. Mishra, S.K. Tiwari(2008), Electrochim.Acta, 53,2322–2330. <https://doi.org/10.1016/j.electacta.2007.09.047>
- [5] U.Balachandran,J.T.Dusek,R.L.Mieville,R.B.Poeppel, M.S.Kleefisch,,S.Pei,T. P. Kobylinski, C. A. Udovich, A. C. Bose(1995), Appl. Catal. A-Gen., (1) 133 19-29. [https://doi.org/10.1016/0926-860X\(95\)00159-X](https://doi.org/10.1016/0926-860X(95)00159-X)
- [6] U. Balachandran, J. T. Dusek , S. M. Sweeney, R. B. Poeppel, R. L. Mieville, P. S. Maiya, M. S. Kleefisch, , S. Pei, , T. P. Kobylinski, C. A. Udovich, (1995) ,Am. Ceram. Soc. Bull.,(1) 74 71-75
- [7] K.T. Lee, A. Manthiram(2006), J. Power Sources, 158 ,1202. <https://doi.org/10.1016/j.jpowsour.2005.10.021>

- [8] L.P.Rivas-Vasquez, J.C.Rendon Angeles, J.L.Rodriguez-Galicia, C.A.Gutiérrez-Chavarria, J.J.Zhu, K. Yanagisawa(2006), J. Europ. Ceram. Soc., 2681-88.
- [9] M.Omari, S. Belaidi, D. Barkat et M. Ouassaf(2005), J. Soc. Alg. Chim.,(2) 15169.
- [10] S.GuillemetFritsch, P.Alphonse, C.Calmet, H.Coradin, P. Tailhades, A.Rousset, C.R(2005), Acad Sc.Paris(8) 219-227.
- [11] M.Bevilacqua, T.Montini, C.Tavagnacco, G.Vicario, P.Fornasiero, M.Graziani(2006), Solid State Ionics, 177 2957.
- [12] P. Duran, J. Tartaj, F. Capel, C. Moure(2004), J. Europ. Ceram. Soc., 24 2619.
- [13] K. Suresh, T.S. Panchapagesan, K.C. Patil(1999), Solid State Ionics, 126, 299.
- [14] Guemache Abderezak and Omari Mahmoud (2015), J.Chem.Soc.Pak., 37, 06.
- [15] P.Melnikov.VANascimento(2013).Journal of Thermal Analysis and Calorimetry, 115 (1), 145-151 doi.org 10.1007/s10973-013-3339-1
- [16] R.N.Singha, Madhua, R.Awasthia, S.K.Tiwarib(2009). Iron molybdates as electrocatalysts for O_2 evolution reaction in alkaline solutions. Int. J. Hydrog. Energy, vol 34,(11), p 4693-4700. <https://doi.org/10.1016/j.ijhydene.2009.04.006>
- [17] C.Wang, Y.Wang, H.Yang, Y.Zhang, H.Zhao(2018). Revealing the role of electrocatalyst crystal structure on oxygen evolution reaction with nickel as an example. Wiley Online Library, vol 14, (40). <https://doi.org/10.1002/sml.201802895>
- [18] W. Zhan, J. Wang, H. Wang, J. Zhang, X. Liu, P. Zhang, M. Chi, Y. Guo, G. Lu, S. Sun, S. Dai, H. Zhu (2017). Crystal structural effect of AuCu Alloy nanoparticles on catalytic CO oxidation. J. Am. Chem. Soc, vol 139, (26), p 8846–8854. <https://doi.org/10.1021/jacs.7b01784>
- [19] Ramírez, P. Hillebrand, D. Stellmach, M.M. May, P. Bogdanoff, S.Fiechter(2014).Evaluation of MnO_x , Mn_2O_3 and Mn_3O_4 electrodeposited films for the oxygen evolution reaction of water. J PhysChem C, vol 118. p 14073-14081. <https://doi.org/10.1021/jp500939d>
- [20] Du J., Zhang T., Cheng F., Chu W., Wu Z(2014), ChenJ.Nonstoichiometric perovskite $\text{CaMnO}_{3-\delta}$ for oxygen evolution electrocatalysis with high activity. I norg Chem, vol 53, p 9106-9114 <https://doi.org/10.1021/ic501631h>