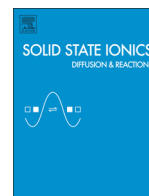




Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Evaluation of aluminium doped lanthanum ferrite based electrodes for supercapacitor design

Atma Rai^{a,*}, A.L. Sharma^b, Awalendra K. Thakur^{a,c}

^a Department of Physics, Indian Institute of Technology, Patna, 800013, India

^b Centre for Physical and Mathematical Sciences, Central University of Punjab, Bathinda, 151001, India

^c Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur, 721302, India

ARTICLE INFO

Article history:

Received 18 May 2013

Received in revised form 8 October 2013

Accepted 10 October 2013

Available online xxx

Keywords:

Supercapacitor

Cyclic voltammetry

EIS

Cycle

Cycle life

ABSTRACT

We report Al doped ferrites $\text{La}_{1-x}\text{Al}_x\text{FeO}_3$ ($x = 0, 0.3$) as an electrode material for supercapacitor design. The $\text{La}_{1-x}\text{Al}_x\text{FeO}_3$ has been synthesized via chemical route. Structural and microstructural evolution has been carried out by X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FESEM) respectively. The electrode property of $\text{La}_{1-x}\text{Al}_x\text{FeO}_3$ has been evaluated by using three electrode systems, glassy carbon (working), Pt (counter) and Ag/AgCl (reference electrode) with H_2SO_4 as the electrolyte. The Al doped ferrites show better cycle life (~250) and columbic efficiency (η) (~96%) in comparison to un-doped lanthanum ferrite sample. An increase in specific capacitance (~1.5 times) has also been observed in Al doped lanthanum ferrite in comparison to lanthanum ferrite. The maximum specific capacitance for Al doped lanthanum ferrite is ~260 F/g as compared to lanthanum ferrite ~200 F/g. The improved specific capacitance, columbic efficiency and cycle life of Al doped ferrites may be related to a relative decrease in equivalent series resistance (95 Ω for LFO to 55 Ω LAFO) and lower M.W. of Al doped lanthanum ferrite.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

At present, fossil fuels are the lifeline for automobiles including surface transport and other utilities. However, they are exhaustible. These sources have a limited lifetime and are polluting environment. So, search for an alternative energy source with features of high energy density, miniaturization and portability is much in demand. Supercapacitors are one such alternative with power storage capacity in the range 20–2000 F/g. Fuel cells, rechargeable batteries and electrolytic capacitors with high specific energy are some other examples of green and clean energy sources [1–10]. Amongst them, supercapacitors are the best alternatives because it offers power density higher than batteries and fuel cell and energy density higher than conventional capacitors. Based on the charge-storage mechanism supercapacitors are classified as; (i) electric double-layer capacitors (EDLC) with capacitive effect arising out of charge accumulation at the electrode electrolyte interface and, (ii) redox supercapacitors having pseudocapacitance, more than ten times greater than EDLC caused by superficial or multi-electron-transfer faradic reactions.

Electrodes with appropriate voltage stability, high surface area and good electronic conductivity play a very crucial role in supercapacitor performance. Multivalent transition metal oxides exhibit excellent pseudocapacitance. Literature reveals that RuO_2 based supercapacitors, though good in performance, suffer from high material cost, while

amorphous MnO_2 based supercapacitors often exhibit poor cycle life. Another serious problem is its poor rate capability, i.e.; lack of sustainability at high discharge rate. In view of these difficulties, we aim to search performance with low cost alternative oxide, having layered structure with capability of fast redox reaction. Perovskite type functional oxides having structural and thermal stability are

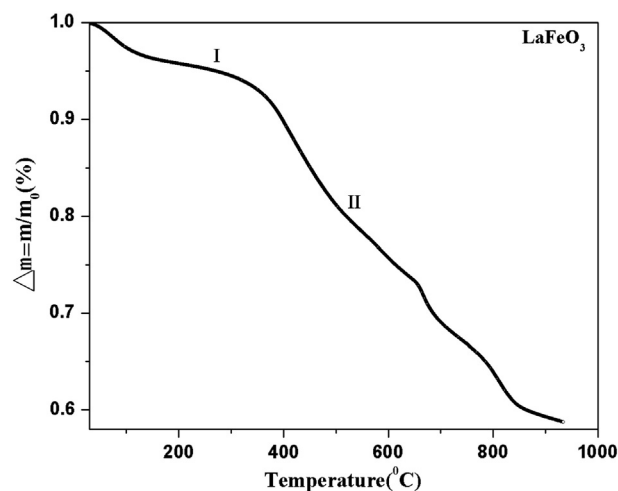


Fig. 1. Thermogravimetric analysis of lanthanum ferrite.

* Corresponding author.

E-mail address: atma@iitp.ac.in (A. Rai).

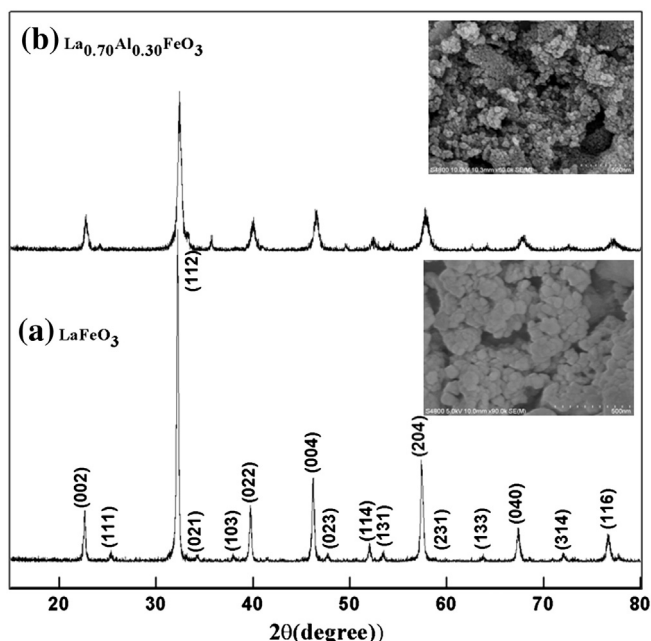


Fig. 2. XRD pattern of (a) LaFeO_3 and (b) $\text{La}_{0.7}\text{Al}_{0.3}\text{FeO}_3$ and FESEM micrograph (inset).

considered to be promising candidates for application as electrode in supercapacitor design.

Present paper reports electrode characteristics of Al based lanthanum ferrite ($\text{La}_{(1-x)}\text{Al}_x\text{FeO}_3$) for supercapacitor applications. The observed experimental results are likely to open a new window of low cost metal oxide with high rate capability and improved electrochemical performance vis-a-vis earlier reports on electrodes [11–19].

2. Experimental procedure

The citrate–nitrate auto ignition method was adopted for the preparation of lanthanum aluminium ferrite (LAFO) powder. Calculated amount of acetates of lanthanum and aluminium and nitrates of iron was dissolved into a small amount of distilled water. The homogeneously mixed solution turned into a gel during heating. The air-dried powder of the parent compound (LaFeO_3 and $\text{La}_{(1-x)}\text{Al}_x\text{FeO}_3$) was calcined at an optimized temperature $\sim 850^\circ\text{C}$ for two hours based on prior optimization using thermogravimetric analysis (TGA) technique. The phase identification/formation of all the prepared ferrite samples was carried out by an X-ray powder diffractometer (model: RIGAKU-TTRAX3) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over a wide range of Bragg's angles (2θ) ($10^\circ \leq 2\theta \leq 80^\circ$) at a resolution of 0.01° . No secondary or impurity phase has been found within error limit of XRD. Field emission scanning electron microscope (FESEM) (model: HITACHI-54800) was employed to record the surface morphology of the sample. Electrochemical measurements were performed on a supercapacitor cell designed using a three electrode cell comprising of glassy carbon (working), platinum (counter) and Ag/AgCl (reference) electrodes. The sample powder was mounted on glassy carbon using NMP as binder and H_2SO_4 (1 M) as an electrolyte. Supercapacitor

performance has been evaluated using CH Instruments (model: CHI 760D). Specific Capacitance (C_s) has been estimated using the relation;

$$C_s = I \times \frac{dt}{dV} \frac{QM}{Fz} \quad (1)$$

I = Current, dv/dt = Slope of charge–discharge curve, Q = Charge, M = molecular weight, F = Faraday constant, z = Electrons transferred per ion.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 shows the thermogravimetric analysis (TGA) pattern of LaFeO_3 (LFO) sample. The thermogram shows two distinct regions of mass loss as marked in Fig. 1. The region I of mass loss begin at 100°C and it continues at a steady rate up to $\sim 350^\circ\text{C}$. It is followed by a steep loss marked as region II suggesting progressive mass loss ($\Delta m/m_0$) with rise in temperature. The gradual loss (region I) up to 350°C may be due to the loss of surface adsorbed moisture during thermal decomposition of precursor compounds. The progressive mass loss (step loss marked as region II) up to $\sim 800^\circ\text{C}$ might be assigned to the thermal oxidative degradation. Beyond 800°C , mass loss becomes stable. The formation temperature of LFO may be $\geq 800^\circ\text{C}$. So, based on this optimization; sample calcination was carried at 850°C for two hours.

3.2. Structural and microstructural analysis

Fig. 2 shows the X-ray diffraction pattern of aluminum doped lanthanum ferrites, $\text{La}_{1-x}\text{Al}_x\text{FeO}_3$ (where $x = 0$, and 0.30) samples. The XRD peaks were indexed as per ICDD file and the lattice parameters were determined in the orthorhombic crystal system using well known Full Prof software. It can be seen from the Fig. 2(a) and (b) that the Al doped lanthanum ferrite ($\text{La}_{(1-x)}\text{Al}_x\text{FeO}_3$) shows identical peaks like LaFeO_3 and main peak has been indexed as [112]. The peak pattern suggests significant degree of polycrystallinity. The lattice constants of lanthanum ferrites are estimated as; $a = 5.5587 \text{ \AA}$, $b = 7.8639 \text{ \AA}$, $c = 5.5484 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ respectively. In addition, the crystallite size is calculated to be $\sim 38 \text{ nm}$ by fitting most intense peak and using Scherrer formula. XRD pattern indicated single phase LFO with orthorhombic crystal structure and Pnma (62) space group. The structural parameters are given in the Table 1.

The surface morphology of $\text{La}_{1-x}\text{Al}_x\text{FeO}_3$ ($x = 0$, and 0.30) is shown in inset of Fig. 2. It is noted that the polycrystalline LFO and LAFO particles (average sizes 40 nm) are uniformly distributed. The smaller particle size of ferrites under study, which is an outcome of the sample processing method, is expected to have larger specific surface area and shorter diffusion pathway for ion migration. For the active material, the smaller particles have larger effective surface area and shorter diffusion distance, which can provide faster mobility, higher material utilization, and improved rate performance.

3.3. Electrochemical analysis

Electrode characteristics of this rare earth based Al doped ferrite have been evaluated with a three electrode system comprising of glassy carbon (working), Ag/AgCl (reference) and Pt (counter) electrode and

Table 1
A comparative structural parameters of LaFeO_3 and $\text{La}_{0.7}\text{Al}_{0.3}\text{FeO}_3$.

System	Crystal structure	a (\AA)	b (\AA)	c (\AA)	$\alpha = \beta = \gamma$ (degree)	V (\AA^3)	Tolerance factor(t)
LaFeO_3	Orthorhombic	5.5587	7.8639	5.5484	90	242.5	0.906
$\text{La}_{0.7}\text{Al}_{0.3}\text{FeO}_3$	Orthorhombic	5.5065	7.8031	5.5514	90	238.5	0.835

Download English Version:

<https://daneshyari.com/en/article/7746159>

Download Persian Version:

<https://daneshyari.com/article/7746159>

[Daneshyari.com](https://daneshyari.com)