

Investigation of Supercapacitive Behaviour of Electrodeposited Cobalt Oxide Thin Film by Potentiostatic Mode

S.S. Gavande^{1,2,*}, Y.H. Navale³, A.S. Salunkhe³, Shivani Gavande³, P.S. Kulkarni⁴, B.R. Karche²

¹ Department of Physics, Sangameshwar College, 413003 Solapur (M.S.), India

² Department of Physics, Shankarrao Mohite Mahavidyala, Akluj, Dist. Solapur (M.S.), India

³ Functional Materials Research Laboratory, School of Physical Sciences, P.A. Holkar Solapur University, 413255 Solapur (M.S.), India

⁴ S.E.S. Polytechnic College, Samrat Chowk Solapur, (M.S.), India

(Received 12 February 2020; revised manuscript received 15 April 2020; published online 25 April 2020)

Cobalt oxide films were prepared potentiostatically on stainless steel substrates. The as-deposited Co_3O_4 films were annealed at 400 °C, 500 °C, 600 °C and were analyzed. The structural analysis of films was carried out by X-ray diffraction technique and wettability parameters by Contact angle measurements at different annealed temperatures. The electrochemical supercapacitive behaviour of Cobalt oxide thin film was studied through Electrochemical properties using cyclic voltammetry and galvanostatic charge-discharge analysis which were carried out in 1 M aqueous KOH, 1 M aqueous NaOH and 1 M aqueous Na_2SO_4 electrolytes at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$ with a three-electrode cell at different annealed temperatures. The film exhibited maximum specific capacitance of 284.4 Fg^{-1} at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$, specific energy 4.325 Whkg^{-1} , specific power 3 kWkg^{-1} and coulomb efficiency 53.75 % in 1 M Na_2SO_4 electrolyte at optimized annealed temperature of 500 °C. In 1 M KOH electrolyte specific capacitance of Cobalt oxide electrode was 182.03 Fg^{-1} at a scan rate 5 $\text{mV}\cdot\text{s}^{-1}$, specific energy 3.570 Whkg^{-1} , specific power 2.00 kWkg^{-1} annealed at 500 °C. In 1 M NaOH electrolyte, annealed at 500 °C, the specific capacitance of Cobalt oxide electrode was 176.33 Fg^{-1} at a scan rate 5 $\text{mV}\cdot\text{s}^{-1}$, specific energy 4.37 Whkg^{-1} , specific power 2.33 kWkg^{-1} .

Keywords: Cobalt oxide, Electrodeposition, Thin films, Cyclic voltammetry, Supercapacitor, Charge-discharge.

DOI: [10.21272/jnep.12\(2\).02011](https://doi.org/10.21272/jnep.12(2).02011)

PACS numbers: 81.15.Pq, 82.47.Uv

1. INTRODUCTION

Nowadays, Supercapacitors have attracted the attention of most researchers widely as they are feasible energy storage devices with high power density, fast charge-discharge rate, and long cycle life. Supercapacitors are intermediate systems that bridge the power/energy gap between traditional dielectric capacitors (high power output) and batteries (high energy-storage) [1]. So, today researchers feel the need of the hour to develop eco-friendly electrode material which is cheap, highly efficient with long life and high storage capacity. Ruthenium and iridium oxides are efficient transition metal oxides but are rare and cause high cost restriction [2]. Therefore, metal oxides such as NiO, MnO_2 , SnO_2 , Co_3O_4 are comparatively good material options for supercapacitor [3]. The specific surface area (SSA) of electrode materials and the properties of electrolytes are key factors of EC electrode material performance, modification of which is very crucial in achieving high power and energy density [4].

Supercapacitor electrode materials are of three types like carbon, metal oxides and polymers. Among these metal oxides, Park et al reported [5] electrodeposited RuO_2 films revealed specific capacitance 788 F/g , Liu et al. reported intercalative pseudocapacitance of Co_3O_4 and CoO_x make them promising electrode materials for supercapacitors [6], while Lin et al. reported using CoO_x xerogelcalcined at 150 °C a maximum capacitance of 291 F/g [7]. Srinivasan and Weidner used Co_3O_4 film as a

positive electrode which exhibited capacitor-like behaviour [8], while Wang et al. reported $\text{Co}(\text{OH})_2$ electrode to show a maximum capacitance of about 280 F/g [9]. The cobalt oxide electrode has good efficiency and long-term performance with good corrosion stability [10]. Various methods such as spray pyrolysis, sputtering, chemical vapor deposition (CVD), pulse laser deposition, sol-gel process, electrodeposition etc. have been used to deposit Cobalt oxide thin film on variety of substrates [11, 12]. The electrodeposition method is very simple, reliable, cost effective, accurate method of electrode deposition. The specific capacitance of the as-deposited Co_3O_4 film obtained was found to be greater than that reported in [13-15] and the specific energy so obtained was found to be greater than that reported in [13].

2. EXPERIMENTAL DETAILS

2.1 Preparation of Cobalt Oxide Thin Film Electrode

The Cobalt oxide thin films were deposited onto stainless steel substrates. The stainless-steel substrates were polished with zero grade polish paper and washed with double-distilled water in an ultrasonic bath for about 15 min. An aqueous solution of 0.1 M Cobalt acetate was used as the precursor for deposition of Cobalt oxide thin film by Potentiostatic mode of Electrodeposition at room temperature (300 K). The as-deposited electrode was annealed at 400 °C, 500 °C and 600 °C.

* shubhangi.gavande15@gmail.com

The crystal structure of cobalt oxide thin films was investigated by X-Ray diffraction technique. Contact angle was measured for wettability study. Electrochemical observations were done using a three-electrode system with cobalt oxide as a working electrode, a platinum electrode as a counter electrode and saturated calomel electrode (SCE) as the reference electrode. The electrochemical experimentation was done at room temperature and all potential values were referred to saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

The crystal structure of Cobalt oxide thin film was investigated by X-Ray diffraction technique. The typical X-ray diffractogram of Cobalt oxide thin film deposited by Potentiostatic mode of electrodeposition annealed at 400 °C, 500 °C, and 600 °C is illustrated in Fig. 1. The diffractogram displays prominent diffraction peaks of Cobalt oxide at 2θ values 20.05°, 31.18°, 36.68°, 38.45°, 44.58°, 52.19°, 59.15°, 65.06°, 77.13° with (111), (220), (311), (222), (400), (422), (511), (440), (533) planes of Cobalt oxide crystal lattice respectively. The diffraction peaks are in close accordance with each other at the three different annealed temperatures i.e. indicating no structural change in the material though annealed at different temperatures namely 400 °C, 500 °C, and 600 °C. The only change due to different annealed temperatures is the diffraction peaks are sharp and fine with greater diffraction intensities with nearly same diffraction angles which are most remarkable at 500 °C, the optimized annealing temperature of electrode than at 400 °C and 600 °C annealing temperatures. Only Co_3O_4 phases with no diffraction peaks corresponding to CoO or Co phases are seen which confirms the formation of pure cubic Co_3O_4 structure with a preferred orientation of (400) crystal plane [16].

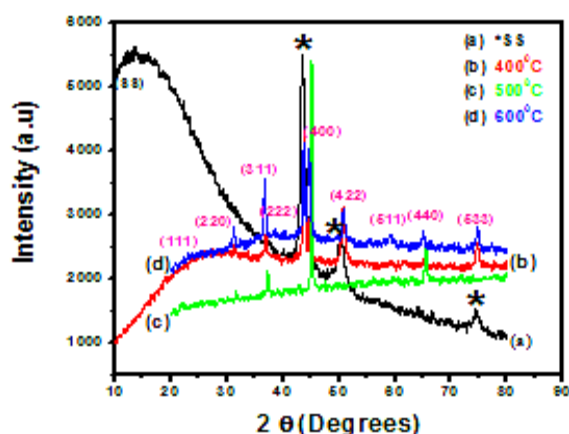


Fig. 1 – XRD pattern of Cobalt oxide thin film

The prominent sharp peaks in the diffractogram are in good agreement with (JCPDS Card No.: 42-1467) and (JCPDS Card No.: 78-1970) with lattice constant $a = 8.0312 \text{ \AA}$ and interplanar spacing $d = 2.0078 \text{ \AA}$, which match with the standard values and confirm the nanocrystalline nature of the deposited Cobalt oxide material. The peak intensity was found to be maximum

at $2\theta = 44.58^\circ$ with (400) plane. Therefore, the average crystallite size of Co_3O_4 film was calculated along (400) plane using Scherrer relation:

$$D = K\lambda / \beta \cos\theta, \quad (1)$$

where, D – crystallite size, K – Scherrer constant (usually 0.89), λ – wavelength of the X-ray radiation (for $\text{CuK}\alpha = 0.1540 \text{ nm}$), β = Full width half maximum (FWHM) of diffraction peak measured at 2θ .

The crystallite size of the most intense prominent peak ($2\theta = 45.58^\circ$) was found to be 5.553 nm (at 400 °C and 600 °C annealing temperature) and the crystallite size of the most intense prominent peak ($2\theta = 46.5^\circ$) was found to be 7.391 nm at 500 °C annealing temperature.

3.2 Surface Wettability Study

Hydrophilic nature of electrode surface indicates prominent wettability i.e. strong cohesive force between oxide from cobalt oxide and water droplet. This property of high wettability causes close contact of the electrolyte with the electrode surface. Hydrophilic exterior of the electrode surface is one of the required features for better supercapacitive performance of the electrochemical capacitors [17].

Hydrophilicity property is necessary for intercalation of charges at the electrode-electrolyte interface which enhances the supercapacitive property of electrode materials in supercapacitive applications. Fig. 2 illustrates the water contact angle measurement on Cobalt oxide thin film surface. The measured water contact angles were 101° at 400 °C, 87° at 500 °C and 101° at 600 °C annealed temperatures respectively, which confirms the hydrophilic behaviour of the as-deposited Cobalt oxide material at 500 °C annealed temperature. The deposited material shows comparatively smaller contact angle of 87° at 500 °C than at 400 °C (101°) and 600 °C (100°) annealing temperature, indicating more hydrophilic nature of the deposited material at 500 °C, the optimized annealing temperature.

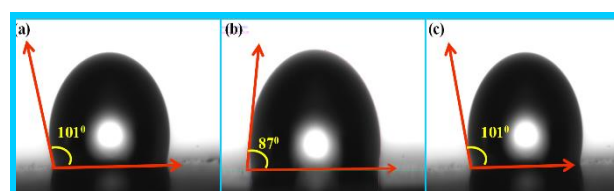


Fig. 2 – Contact angle of Cobalt oxide thin film at annealed temperature 400 °C (a), 500 °C (b), 600 °C (c)

3.3 Surface Morphological Studies

SEM images of a potentiostatically electrodeposited Cobalt oxide electrode annealed at 400 °C, 500 °C and 600 °C are displayed in Fig. 3. Fig. 3a shows the image of Cobalt oxide electrode when annealed at 400 °C. The surface appears highly spongy with empty pores uniformly distributed over the entire surface. There is dark columnar fold like structures appearing embedded in the highly spongy surface resulting in profound increase in the surface area of the electrode. This may help to host large number of charges which may result an increase in capacitance of the electrode.

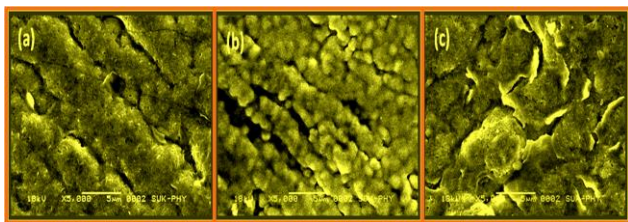


Fig. 3 – SEM images of Cobalt oxide thin film at annealed temperature 400 °C (a), 500 °C (b), 600 °C (c)

The SEM image of Cobalt oxide electrode annealed at 500 °C is displayed in Fig. 3b. The increase in annealing temperature has resulted in granular cluster formation due to agglomeration of nanoparticles at the empty pores uniformly distributed over the entire surface retaining the vertical folds unaffected. Further increase in the annealing temperature above the optimized temperature i.e. above 500 °C the place of cluster of nano size granular particles is taken by spongy nanoflake islands of deposited material. This abundant porous structure should benefit the charge exchange and ionic transportation in the Cobalt oxide supercapacitor electrode.

Confirmation of formation of porous Co_3O_4 the elemental compositional mapping was done through the profile spectrum obtained by EDAX analysis at 400 °C, 500 °C and 600 °C annealing temperatures of the as-deposited Co_3O_4 electrode. The Figures, Fig. 4a, b and c illustrate the element and weight percentage contribution of Co and O in the formation of cobalt oxide respectively. The presence of peaks of Co and O elements in the profile spectrum confirms the formation of cobalt oxide namely Co_3O_4 . The profile chart shows the weight percentage of Co (69.42 Wt %) and O (25.78 Wt %) at 400 °C, Co (73.24 Wt %) and O (23.96 Wt %) at 500 °C and Co (62.61 Wt %) and O (23.85 Wt %) at 600 °C annealing temperature of the deposited electrode respectively. The weight percentage contribution of Co (73.24 Wt %) and O (23.96 Wt %) is found to be higher at the optimized annealing temperature 500 °C.

3.4 Supercapacitive Properties of Cobalt Oxide Electrode

Investigation of supercapacitive behaviour of Cobalt oxide electrode was done by Cyclic voltammetry (CV) at different scan rates in aqueous 1 M KOH, 1 M NaOH and 1 M Na_2SO_4 electrolyte. Electrochemical analyzer was used to conduct cyclic voltammetry with saturated calomel electrode as the reference electrode, a platinum wire as counter electrode and stainless steel as working electrode. The specific capacitance was calculated from cyclic voltammetry.

The as-deposited Cobalt oxide thin film electrode was annealed at three different temperatures 400 °C, 500 °C, and 600 °C. These thin films on heat treatment are found to alter their water content and their crystalline nature. The annealing temperature does have effect on the electrochemical properties of the electrode with slight change in its microstructures. The capacitance of thin film electrode is found to change with annealing temperatures. The Specific capacitance of the thin film Cobalt oxide electrode is found to increase

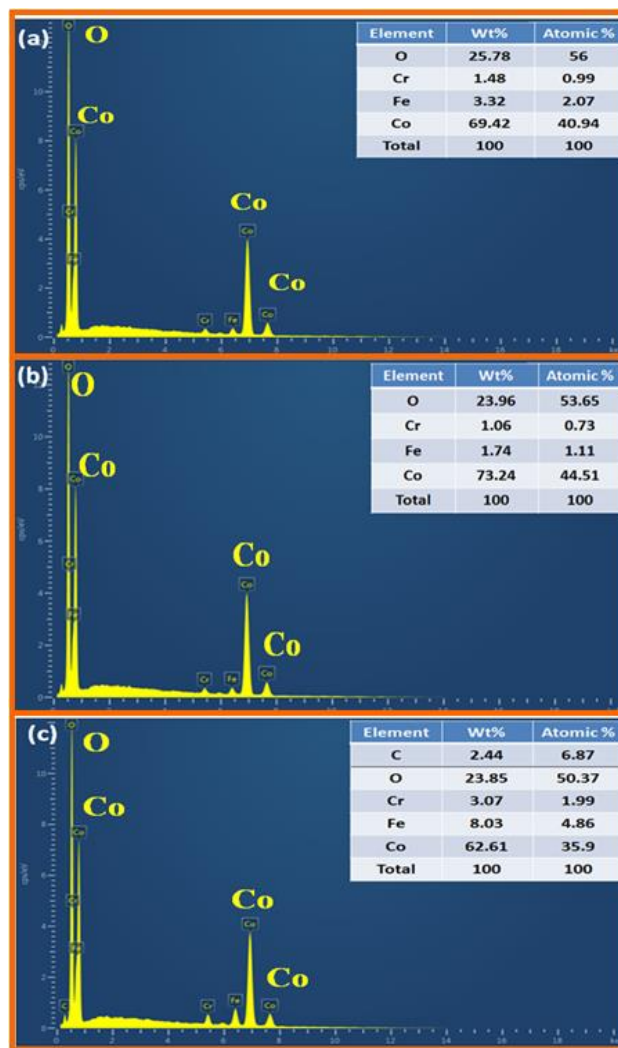


Fig. 4 – EDAX spectrum of Co_3O_4 electrode with inset table showing wt % of Co and O elements at annealed temperature 400 °C (a), 500 °C (b), 600 °C (c)

with the increase in annealing temperature to a maximum of about 182.03 F/g in 1 M KOH, 284.4 F/g in 1 M Na_2SO_4 and 176.33 F/g in 1 M NaOH electrolyte, which then substantially decreases with increase in annealing temperature which is in agreement with the observations reported by Srinivasan and Weidner [8].

CV of Cobalt oxide thin film electrode in 1 M KOH at three different annealing temperatures is shown in Fig. 5a. The plot shows well resolved oxidation peak at 0.43 V and reduction peak at 0.39 V. The oxidation peak signifies the formation of Cobalt hydroxide simultaneously the reduction peak signifies the conversion of oxy-hydroxide back to hydroxide. Apart from the apparent oxidation-reduction peaks, the voltammogram shows that as the film is cycled from 0 towards the anodic direction, a purely capacitive current is obtained between 0 and 0.49 V. This suggests that a reversal of the CV at 0.49 V may give a voltammogram that is purely due to the capacitance of the film rather than due to the redox (faradaic) reaction peaks observed in Fig. 5a [18]. The annealing temperature brings about change in the capacitance of the electrode which is estimated from the area under the I - V curve shown in

Fig. 5b and c. The surface charge density ($q\text{cm}^{-2}$) is equal to integration of the area under the I - V curve and is proportional to the capacitance of the film since:

$$C(V_f - V_i) = q = \frac{1}{\nu} \int_{V_i}^{V_f} I(V) dV, \quad (2)$$

where C is the total capacitance, I – the current density (A/cm^2), ν – the sweep rate (V/s), V_i – the initial and V_f – the final voltages (V).

The integral on the right hand side of above equation is the area under the C - V curve. Thus, the total

surface charge, (or total capacitance) of the deposited material can be estimated by evaluating the area under the capacitive current-voltage curve portion of a C - V (without faradaic reaction peaks) [18].

Decrease in specific capacitance with Scan rate at different annealing temperatures in 1 M KOH, 1 M Na_2SO_4 and 1 M NaOH electrolyte respectively, is shown in Fig. 5d, Fig. 5e and Fig. 5f. The rate of decrease of Specific capacitance is remarkable at scan rate from $5 \text{ mV}\cdot\text{s}^{-1}$ to $25 \text{ mV}\cdot\text{s}^{-1}$ which is slower beyond $25 \text{ mV}\cdot\text{s}^{-1}$ to $100 \text{ mV}\cdot\text{s}^{-1}$ in all the three electrolytes.

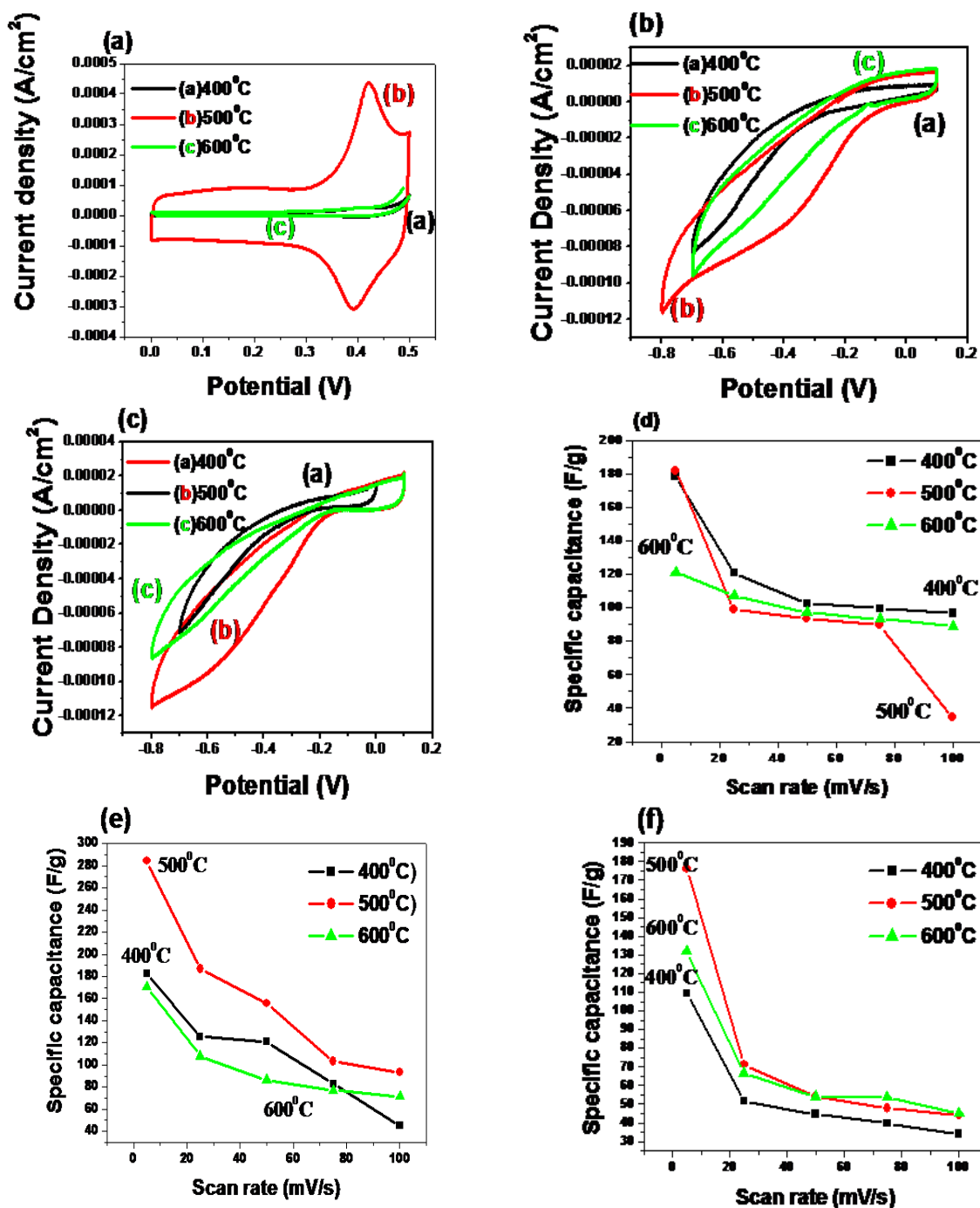


Fig. 5 – Cyclic voltammetry of Co_3O_4 electrode at 400°C , 500°C , and 600°C in 1 M KOH (a), 1 M Na_2SO_4 (b), 1 M NaOH (c) with $5 \text{ mV}\cdot\text{s}^{-1}$ Scan rate. Variation of Specific capacitance with Scan rate at different annealing temperatures in 1 M KOH electrolyte (d), 1 M Na_2SO_4 electrolyte (e) and 1 M NaOH electrolyte at different annealing temperatures (f)

The average decrease in specific capacitance with scan rate is much smaller in 1 M Na₂SO₄ and 1 M NaOH especially at 500 °C as compared to 1 M KOH electrolyte respectively. This shows that at 500 °C the stability of capacitance of the as-deposited material is much higher in 1 M Na₂SO₄ (82 %) and 1 M NaOH (83 %) than in 1 M KOH electrolyte (79 %) respectively. This inference well explains that in the present deposition 500 °C is an optimal temperature of annealing. The corollary is that at a specific annealing time and an optimal temperature the hydroxide film is annealed completely to an oxide film without sintering. At this specific annealing time and optimal temperature, all the oxide's properties are enhanced and the film shows maximum capacitance with the anodic and cathodic peaks of the oxide's cyclic voltammogram are equal and at their minima [18].

Effect of Electrolytes and Sweep Rates

The effect of scan rate on specific capacitance of Cobalt oxide electrode was studied in 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes. The CV curves for the cobalt oxide electrode in the three electrolytes with different scan rates were plotted. The CV plots of Co₃O₄ electrode at scan rates from 5 mV·s⁻¹ to 100 mV·s⁻¹ in potential window from 0.0 V to 0.5 V in aqueous 1 M KOH electrolyte are illustrated in Fig. 6a. The plots show increase in the area of the C-V curve with increase in the scan rate. In this plot of C-V curves the electrodes exhibit two pairs of redox peaks, indicating the origin of capacitance via Co₃O₄ electrodes which have primarily resulted from the faradaic pseudocapacitance in an alkaline electrolyte [16]. The C-V plots of Co₃O₄ electrode at scan rates from 5 mV·s⁻¹ to 100 mV·s⁻¹ in potential window from -0.8 V to 0.1 V in aqueous 1 M Na₂SO₄ electrolyte are displayed in

Fig. 6b. The C-V plots of Co₃O₄ electrode at scan rates from 5 mV·s⁻¹ to 100 mV·s⁻¹ in potential window from -0.8 V to 0.1 V in aqueous 1 M NaOH electrolyte are shown in Fig. 6c. Importantly, the redox current increases continuously with the increase of scan rate and well-defined pair of redox peaks with different scan rates affirms that the capacitance is dominated by the Faradic reaction [19]. The current under the curve increases slowly with the scan rate. This shows that the voltammetric current is directly proportional to the scan rate of C-V, indicating an ideally capacitive behaviour [20].

The specific capacitance was found to decrease with scan rate. The decrease in capacitance with the scan rate is attributed to the presence of inner active sites, which cannot precede the redox transitions completely at higher scan rates of C-V, probably due to the diffusion effect of proton within the electrode. The decreasing trend of the capacitance suggests that the parts of the surface of electrode are inaccessible at high charging-discharging rate. Hence, the specific capacitance obtained at the slowest scan rate is believed to be close to that of full utilization of the electrode material [20].

Variation in specific capacitance at scan rate of 100 mV/s for 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes is displayed in Fig. 6d. It is also observed that the C-V curve of Co₃O₄ electrode in 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes shows the area under the curve for Na₂SO₄ electrolyte covers a larger area indicating higher Specific capacitance than for KOH and NaOH electrolyte. Maximum value of specific capacitance for Co₃O₄ film electrode was 284.4 F/g (1 M Na₂SO₄) > 182.64 F/g (1 M KOH) > 176.33 F/g (1 M NaOH) electrolyte at the sweep rate of 5 mV·s⁻¹, which could be due to the differences in the ion diffusion coefficients of Na⁺ and K⁺ ions have diameters of ~ 0.95 Å and 1.33 Å respectively [21].

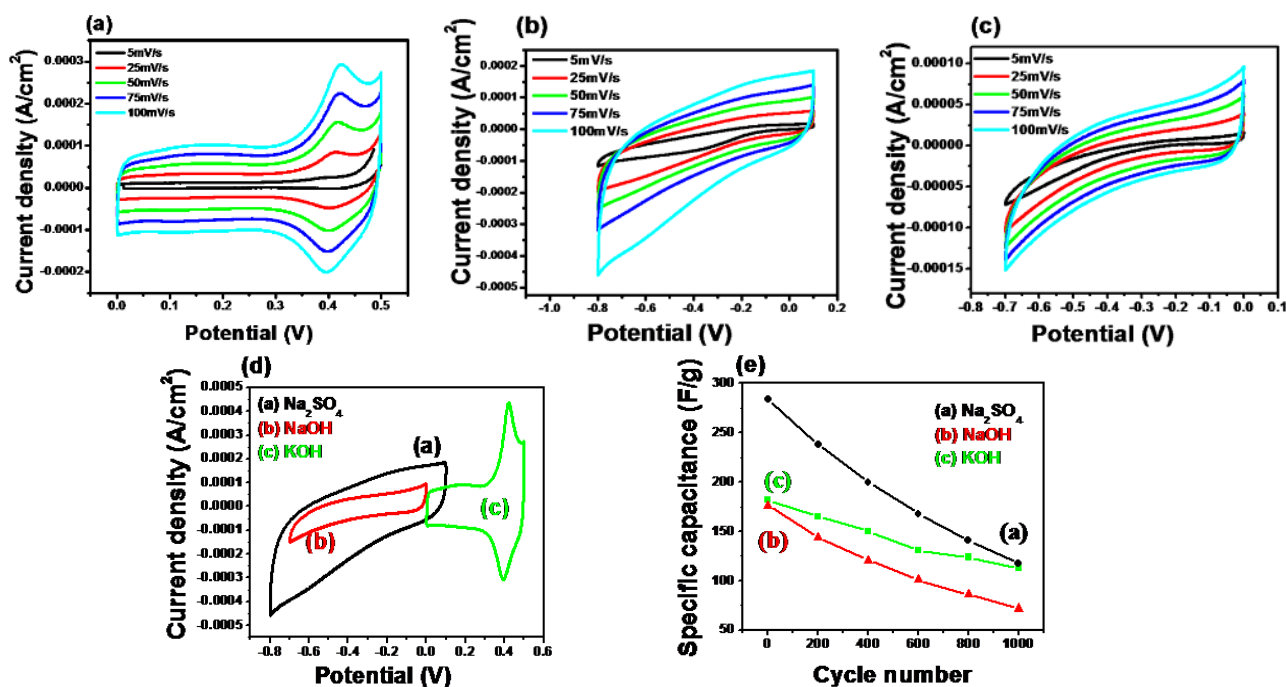


Fig. 6 – Cyclic voltammetry of Co₃O₄ electrode in 1 M KOH (a), in 1 M Na₂SO₄ (b), in 1M NaOH (c) and Combine C-V in 1 M KOH, 1 M Na₂SO₄, 1 M NaOH at 100 mV·s⁻¹ (d). Scan rate at 500 °C annealing temperature variation of specific capacitance with cycle number (e)

The dependency between specific capacitance and molar conductivity showed that the high molar conductivity leads to high specific capacitance [22, 23]. During the effect of sweep rates study, the decrease in specific capacitance of electrode at higher sweep rates was noticed. It may be caused due to outer regions of the electrode material are being accessed by the electrolyte, while at lower sweep rates, the whole electrode material can be utilized for charge migration (i.e. allows sufficient time for the electrode material for reduction) [24].

The supercapacitive property of the electrode is also found to change with the change in electrolyte. Here in the present study three electrolytes aqueous 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes were used. The electrolyte containing salt and solvent is considered as one of the key factors of electrochemical studies, providing ionic conductivity and thus facilitating charge compensation on each electrode in the cell [12]. This is associated with increase in current response in the C-V profiles that indicates good capacitive behaviour [22]. The C-V of the supercapacitor displays change in current at each end potential of which indicates pseudo capacitive behaviour [23]. The C-V profiles did not display the conventional electric double layer capacitive behaviour (ideal rectangular shape). From C-V curves, it is seen that the capacitance is mainly due to the redox reactions between the electrode and electrolyte [22, 25]. Variation of specific capacitance with cycle number which directly relates stability of the electrode material in the different electrolytes is displayed in Fig. 6e. The rate of decrease of specific capacitance with cycle number i. e. cycle life of electrode material is comparatively similar in all the three electrolytes. Exact comparison from the rate of decrease of specific capacitance it would be stated as the cycle life of electrode material is better in 1 M NaOH electrolyte (83.36 %), than 82.70 % in 1 M Na₂SO₄ and 79.25 % in 1 M KOH electrolyte. The Capacitance(C) and Specific

capacitance (SC) of the as-deposited Cobalt oxide electrode in aqueous 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes was calculated at 400 °C, 500 °C and 600 °C annealing temperatures and the detail findings are summarized in Table 1.

Table 1 – Tabulation of findings of the research work

Sr. No	Temperature	Electrolyte	Capacitance (F cm ⁻²)	Specific Capacitance (Fg ⁻¹)
1	400 °C	KOH	0.0447	178.62
		Na ₂ SO ₄	0.0457	182.64
		NaOH	0.0129	109.12
2	500 °C	KOH	0.0546	182.03
		Na ₂ SO ₄	0.0715	284.40
		NaOH	0.0529	176.33
3	600 °C	KOH	0.0316	121.54
		Na ₂ SO ₄	0.0443	170.42
		NaOH	0.0343	132.08

Charge-Discharge Study

The cyclic stability of Co₃O₄ was studied by galvanostatic charge discharge analysis. The charge-discharge operation of Cobalt oxide electrode was examined by galvanostatic charge-discharge method in 1 M KOH, 1 M NaOH and 1 M Na₂SO₄ electrolytes as illustrated in Fig. 7a, b and c. Discharge curves in 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH for 1 mAcm⁻² Current density is displayed in Fig. 7d. The discharge time is found to be comparatively longer in 1 M KOH electrolyte about $T_d = 6.916$ s, in 1 M NaOH $T_d = 6.738$ s and in 1 M Na₂SO₄ $T_d = 5.1897$ s respectively. The discharge profile usually contains two parts, first a resistive component arising from the sudden voltage drop representing the voltage change due to the internal resistance and a capacitive component related to the voltage change due to change in energy within the capacitor [26].

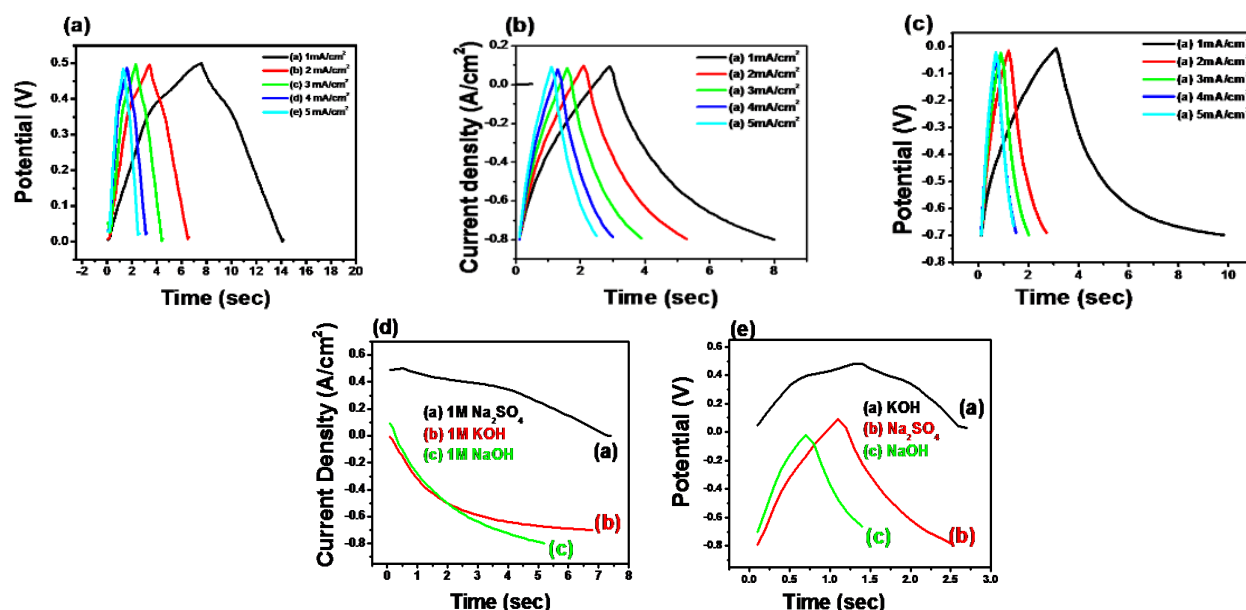


Fig. 7 – Charge discharge curves of Co₃O₄ electrode in 1 M KOH (a), in 1 M Na₂SO₄ (b), in 1 M NaOH (c), discharge curves in 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH for 1 mAcm⁻² current density (d). CD measurement at 5 mAcm⁻² current density for 1 M KOH, 1 M Na₂SO₄ and 1 M NaOH electrolytes (e)

Discharge curves of Co_3O_4 electrode in 1 M KOH, 1 M Na_2SO_4 and 1 M NaOH electrolytes at 5 mAcm^{-2} current density is represented in Fig. 7d and Fig. 7e. The charge profile is found to be non-linear indicating pseudocapacitive property of Co_3O_4 electrode. It can be seen that the charge profile is nonlinear, suggesting a pseudocapacitive characteristic. At the time of electric current reversing from charging to discharging, a potential drop is observed because of the electrode polarization at this high current rate [27]. A discharge cycle is formed of two slopes, one that is parallel to voltage axis indicating the voltage drop and the other slope representing the capacitive behaviour [28]. It is seen at optimized annealing temperature i.e. 500°C of the Co_3O_4 electrode, it is observed that the discharge time is higher than the charging time for Co_3O_4 electrode in all the three electrolytes. Therefore, efficiency was calculated by taking the ratio of $(T_d/T_c) \times 100$ instead of $(T_c/T_d) \times 100$ as the ratio exceeded 100 %. Hence the efficiency is practically found to be very high at optimized annealing temperature in all the three electrolytes.

The stability or cycle life of Cobalt oxide electrode in different electrolytes was evaluated from C-V curve. The curves of NaOH, Na_2SO_4 and KOH electrolytes respectively, reveal decrease in SC value with increase in cycle numbers. After 1000th cycles the capacitance retention ratio (capacitance at the 1000th cycle/ capacitance at the 1st cycle) was 79.25 % in KOH, 82.70 % in Na_2SO_4 and 83.36 % in 1 M NaOH electrolyte. The current under the C-V curve was found to decrease by 1.26 times (approx. 20 %) up to 1000 cycles in 1 M KOH, in 1 M NaOH electrolyte 1.2 times (approx. 17 %) up to 1000 cycles and 1.199 times (approx. 17 %) in 1 M Na_2SO_4 electrolyte. These inferences show that as-deposited Cobalt oxide electrode can operate for 1000 cycles without significant decrease in capacitance hence showing remarkable stability in energy storage usage. The calculated electrochemical parameters are summarized in Table 1. All these inferences indicate Cobalt oxide electrode shows maximum specific capacitance with longer stability and hence functions as a promising electrode material for high performance energy storage systems. The Specific energy (SE), Specific power (SP) and Coulomb Efficiency (η) was calculated and the details are summarized in Table 2.

Table 2 – Supercapacitive parameters of Co_3O_4 thin film electrode at 5 mVs^{-1} and 1 mAcm^{-2} current density

Sr. No	Temperature	Electrolyte	Specific Energy (Whkg ⁻¹)	Specific Power (kWkg ⁻¹)	Coulomb Efficiency (%)
1	400 °C	KOH	3.202	1.67	94.33
		Na_2SO_4	1.084	3.20	73.19
		NaOH	1.743	3.60	71.72
2	500 °C	KOH	3.570	2.00	91.24
		Na_2SO_4	4.325	3.00	53.86
		NaOH	4.367	2.33	44.95
3	600 °C	KOH	3.439	1.92	85.64
		Na_2SO_4	2.602	3.08	65.76
		NaOH	1.712	3.46	80.64

Electrochemical Impedance Spectroscopy Study

Electrochemical impedance spectroscopy study is a massive tool to evaluate the frequency behaviour and equivalent series resistance (ESR) of electrochemical supercapacitors. [29]. Nyquist plot is a graph of real part of impedance (Z') versus the imaginary part of impedance ($-Z''$). Fig. 8 illustrates the Nyquist plots of Cobalt oxide film electrode in the three electrolytes which are mostly similar. The semicircle at higher frequency region is ascribed to charge transfer process at electrode/electrolyte interface, and the straight line at low-frequency region indicates diffusive resistance [30]. The greater the slope of the low frequency line, nearer is the behaviour of electrode to the ideal supercapacitor, which means enhanced electrocapacitive behaviour [31, 32].

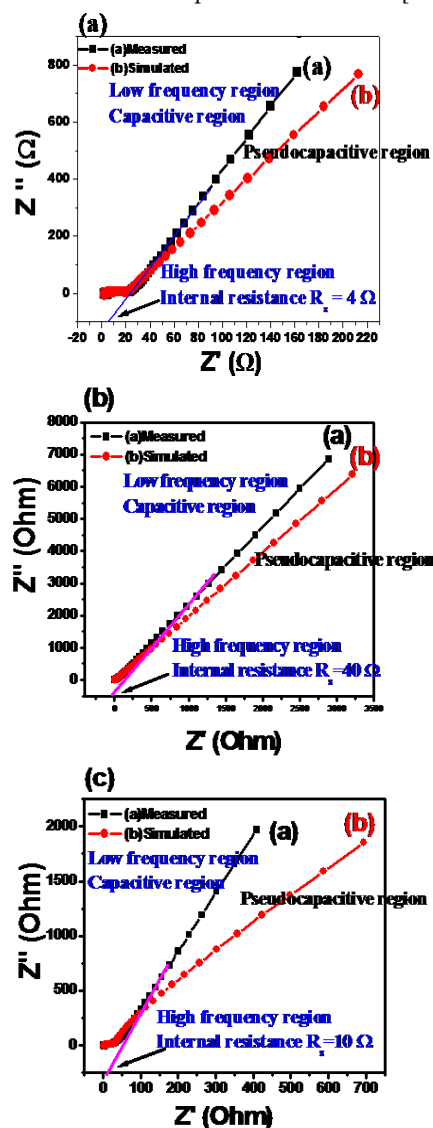


Fig. 8 – Nyquist plots of Co_3O_4 electrode in 1 M KOH (a), 1 M Na_2SO_4 (b), 1 M NaOH (c)

4. CONCLUSION

The present research exploration reports a simple, cost effective electrochemical method for electrodeposition of high-performance supercapacitor Cobalt oxide (Co_3O_4) electrode by Potentiostatic mode. The structure of the film was confirmed by XRD and Raman tech-

niques. The film had a highly porous, spongy, columnar fold, cluster morphology suitable for supercapacitor application. The measured Contact angle of 101° at 87°C and 101° at 400°C , 500°C and 600°C attributed Cobalt oxide electrode surface to be hydrophilic in nature. The electrochemical analysis revealed that the Co_3O_4 electrode exhibited a maximum Specific capacitance of 284.4 Fg^{-1} at a scan rate of 5 mVs^{-1} , specific energy 4.325 Whkg^{-1} , specific power 3 kWkg^{-1} and coulomb efficiency was 53.86% in $1\text{ M Na}_2\text{SO}_4$ aqueous electrolyte at 500°C optimized temperature. In 1 M aqueous KOH electrolyte the electrode showed maximum Specific capacitance of about 182.03 Fg^{-1} at a scan rate 5 mVs^{-1} , Specific energy 3.570 Whkg^{-1} and Specific power 2.00 kWkg^{-1} at 500°C optimized temperature. In 1 M NaOH electrolyte the electrode showed maximum Specific capacitance of about 176.33 Fg^{-1} at a scan rate 5 mVs^{-1} , Specific energy 4.37 Whkg^{-1} and Specific power 2.33 kWkg^{-1} at 500°C optimized temperature. After 1000^{th} cycles the

capacitance retention ratio for Cobalt oxide thin film electrode was 79.25% in KOH, 82.70% in Na_2SO_4 and 83.36% in 1 M NaOH electrolyte. All these observations prove that Cobalt oxide electrode has superior supercapacitive behaviour and has huge potential application in electrochemical supercapacitors.

ACKNOWLEDGMENTS

The authors would like to express their deep gratitude to Prof. V B Patil, Director of Physical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur, Maharashtra, India, for providing required laboratory facilities, their kind cooperation and support in completing this research work. The authors would also like to acknowledge their gratitude to Sophisticated Test and Instrumentation Centre, Kochi University 682022, Kerala, India, for their prompt, accurate and valuable cooperation in performing SEM-EDAX analysis of the research samples.

REFERENCES

1. X. Liu, P.G. Pickup, *Energ. Environ. Sci.* **1**, 494 (2008).
2. P. Jampani, A. Manivannan, P.N. Kumta, *Electrochem. Soc. Interface* **19**, 57 (2010).
3. I.A. Dhole, Y.H. Navale, C.S. Pawar, S.T. Navale, V.B. Patil, *J. Mater. Sci.: Mater. Electron.* **29**, 5675 (2018).
4. T. Katakabe, T. Kaneko, M. Watanabe, T. Fukushima, T. Aida, *J. Electrochem. Soc.* **152**, A1913 (2005).
5. B.O. Park, C.D. Lokhande, H.S. Park, *J. Power Source.* **134**, 148 (2004).
6. T.C. Liu, W.G. Pell, B.E. Conway, *Electrochim. Acta* **44**, 2829 (1999).
7. C. Lin, J.A. Ritter, B.N. Popov, *J. Electrochem. Soc.* **145**, 4097 (1998).
8. V. Srinivasan, J.W. Weidner, *J. Power Source.* **108**, 15 (2002).
9. Wang, Xiao-Feng, You Zheng, Ruan Dian-Bo, *Chinese J. Chem.* **24**, 1126 (2006).
10. H. Kim, T. Seong, J. Lim, W. Cho, *J. Power Source.* **102**, 167 (2001).
11. Y.H. Navale, S.T. Navale, I.A. Dhole, *Org. Electron.* **57**, 110 (2018).
12. K.R. Prasad, N. Miura, *J. Power Source.* **135**, 354 (2004).
13. A.D. Jagadale, V.S. Kumbhar, R.N. Bulakhe, C.D. Lokhande, *Energy* **64**, 234 (2014).
14. S.G. Kandalkar, D.S. Dhawale, Chang-Koo Kim, C.D. Lokhande, *Synthetic Met.* **160**, 1299 (2010).
15. A.D. Jagadale, V.S. Kumbhar, D.S. Dhawale, C.D. Lokhande, *Electrochim. Acta* **98**, 32 (2013).
16. Gwang-Su Jang, S. Ameen, M.S. Akhtar, E. Kim, H. Shin, *J. Mater. Sci.* **2**, 8941 (2017).
17. O. Bockman, T. Ostvold, G.A. Voyiatzis, G.N. Papatheodorou, *Hydrometal.* **55**, 93 (2000).
18. E.E. Kalu, T.T Nwoga, V. Srinivasan, J.W. Weidner, *J. Power Source* **92**, 163 (2001).
19. S. Ardizzone, G. Fregonara, S. Trasatti, *Electrochim. Acta* **35**, 263 (1990).
20. C.D. Lokhande, T.P. Gujar, V.R. Shinde, R.S. Mane, S.H. Han, *Electrochem. Commun.* **9**, 1805 (2007).
21. D. Yan, P. Yan, S. Cheng, J. Chen, R. Zhuo, J. Feng, G. Zhang, Fabrication, *Cryst. Growth Des.* **9**, 218 (2009).
22. P.D. More, I.A. Dhole, Y.H. Navale, S.T. Navale, V.B. Patil, *Solid State Ionic.* **334**, 56 (2019).
23. F. Barzegar, D.Y. Momodu, O.O. Fashedemi, A. Bello, J.K. Dangbegnon, N. Manyala, *RSC Adv.* **5**, 07482 (2015).
24. R.S. Ray, B. Sarma, A. Jurovitzki, M. Mishra, *J. Chem. Eng.* **260**, 671 (2015).
25. S. Patil, S. Raut, R. Gore, B. Sankapal, *New J. Chem.* **39**, 9124 (2015).
26. S.G. Kandalkar, J.L. Gunjekar, C.D. Lokhande, *Appl. Surf. Sci.* **254**, 5540 (2008).
27. C. Xu, B. Li, H. Du, F. Kang, Y. Zeng, *J. Power Source* **180**, 664 (2008).
28. C.Z. Yuan, B. Gao, X.G. Zhang, *J. Power Source.* **173**, 606 (2007).
29. Y.H. Navale, S.M. Ingole, S.T. Navale, F.J. Stadler, R.S. Mane, M. Naushad, V.B. Patil, *J. Colloid Interf. Sci.* **487**, 458 (2017).
30. J. Zhao, B. Tang, J. Cao, J. Feng, P. Liu, J. Zhao, J. Xu, *Mater. Manuf. Process.* **27** No 2, 119 (2012).
31. P.L. Taberna, P. Simon, J.F. Fauvarque, *Electrochem. Soc.* **150** No 3, A292 (2003).
32. V. Ganesh, S. Pitchumani, V. Lakshminarayanan, *J. Power Source.* **158**, 1523 (2006).