

Synthesis, structure and capacitive properties of cobalt hydroxide films on stainless steel substrates

Research Article

Ieva Barauskienė*, Eugenijus Valatka

Department of Physical and Inorganic Chemistry,
Kaunas University of Technology, LT-50254 Kaunas, Lithuania

Received 15 October 2013; Accepted 9 March 2014

Abstract: Cobalt (hydro)oxide films on *AISI 304* stainless steel and sintered metal fibre filter *Bekipor ST 20AL3* were prepared using electrochemical deposition from neutral cobalt acetate solutions under galvanostatic conditions. Deposited films were structurally characterized using X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. All electrochemical measurements were performed in aqueous NaOH solution. Capacitive behavior of different films was evaluated using cyclic voltammetry data. The highest specific capacitance (965 F g^{-1}) was reached when *Bekipor ST 20AL3* mesh was used as a support for electroactive substance.

Keywords: Cobalt hydroxide • Capacitance • Supercapacitors • Metal fibre filters

© Versita Sp. z o.o.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, are considered to be one of the potential energy storage systems in addition to batteries [1-12]. Their unique properties, such as great capacity, quick formation of the high power impulse and ability to provide long shelf life, distinguish this group from many others. Due to these advantages, supercapacitors are already used in many applications such as vehicles, electricity substations, maintenance systems of electronic devices and etc. [13-16]. Compared with the batteries or fuel cells, traditional capacitors allow a high specific power but low specific energy. Batteries are able to save a great amount of energy, but they cannot generate a short, great power impulse; for this purpose capacitors are used [17-25].

The main principle of supercapacitors is very similar to electrostatic ones. Due to the greater surface area (up to $2500 \text{ m}^2 \text{ g}^{-1}$) and smaller distance between electrodes, supercapacitors are able to store much greater amounts of energy. Supercapacitors have much longer cycle life ($\sim 10^6$ cycles) and shorter period of charge accumulation ($\sim 0.6 \text{ s}$) compared with electrochemical batteries or fuel cells. There are three types of supercapacitors based

on electrochemical active materials and the mechanism of charge storage [1]: electrochemical double layer, pseudocapacitors and hybrid capacitors.

Pseudocapacitors store energy by charge transfer between electrode and electrolyte because of the Faradaic reactions, occurring on the surface of active material. In this case capacitance is determined by the electric charge transfer rate which depends on the quantity of active substance and the surface area of transfer. The major properties of supercapacitors are cycling life, self-discharge current, efficiency, specific capacitance, power density and energy density [1]. A lot of materials are used in the production of supercapacitors: ruthenium oxide, active carbon, conducting polymers and oxysulfides [24,25]. However, metal oxides are considered to be the most promising materials for supercapacitors [3]. Among all metal oxides cobalt oxide compounds are great candidates due to their layered structure with large interlayer spacing [4,5].

Sintered metal fiber filter (MFF) is a mechanically and chemically stable composition of thin metal filaments ($d = 2\text{-}30 \mu\text{m}$), usually in the form of panels of different thickness [26]. Because of the small fibre diameter MFFs are used as a support for thin oxide coatings to increase

* E-mail: ieva.barauskiene@ktu.lt

the specific surface area. Micro-fibrous filters are effectively used in the catalytic beds, filtration of solid particles and combustion of gaseous pollutants.

The aim of this work was to investigate structural and capacitive properties of cobalt (hydro)oxide films electrodeposited on different metal substrates.

2. Experimental procedure

2.1. Preparation of the films

Cobalt hydroxide films on stainless steel were prepared by electrochemical deposition using a standard three electrode cell (volume 100 mL). *AISI 304* stainless steel plates, 0.5 mm thick, and *Bekipor ST 20AL3* mesh were used as supports. Sintered metal fibre filter *Bekipor ST 20AL3* in the form of a panel with thickness of 0.49 mm was supplied by Bekaert Fibre Technology (Belgium). This material has a porosity of 81%.

The size of substrate plates was 10×40 mm. All solutions were prepared using doubly distilled water and analytical grade reagents. Cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2$, >97% purity) and potassium nitrate (KNO_3 , purity >99%) were obtained from Reachim (Russia) and used as received. The optimal composition of the solution (0.05 M $\text{Co}(\text{CH}_3\text{COO})_2$ + 0.1 M KNO_3) was determined during previous work [27]. Only freshly prepared solutions (initial pH 7.05) were used for the measurements. Not all solutions were deaerated during the experimental runs. The electrochemical synthesis was carried out at 291 K \pm 1 K. The as-deposited samples were thoroughly washed with distilled water and dried to constant weight at room temperature. The electrodeposition process was carried out under galvanostatic conditions. The obtained results showed that the most stable films were obtained at 0.5 mA cm^{-2} for films on *AISI 304* stainless steel plates and at -4 mA for films on *Bekipor ST 20AL3* mesh. The duration of electrosynthesis of films for capacitance measurements was varied in the range of 1–12 min. The duration of electrodeposition of films for structural analysis was 30 min. Co_3O_4 films were prepared by heating cobalt hydroxide films at 673 K temperature for 3 hours.

2.2. Electrochemical measurements

The electrochemical measurements were performed by a computer-controlled Autolab PGSTAT12 (Ecochemie, The Netherlands) potentiostat/galvanostat using a three-compartment electrochemical cell. The GPES® 4.9 software was used for the collection and treatment of the experimental data. Throughout the paper all potentials are referred to Ag, AgCl | KCl(sat) reference electrode. A platinum wire (geometric area about

15 cm^2) was used as a counter electrode. 0.1 M NaOH (purity >99%, Reachim, Russia) solution was used as a supporting electrolyte. To evaluate the specific capacitance of the films, all cyclic scans were repeated at least ten times. The losses of the specific capacitance were calculated to be around 56% for the first cycle and 1–3% for all the other cycles. According to these losses, the anodic charge value of the 10th cycle was used in calculations.

2.3. Structure analysis

The X-ray powder diffraction (XRD) data were collected with a DRON-6 (Bourestnik Inc., Russia) powder diffractometer with Bragg–Brentano geometry using Ni-filtered Cu K_α radiation and a graphite monochromator. All films were prepared by peeling-off from the support. All scanning electron microscopy (SEM) images were acquired using the Hitachi S-4800 scanning electron microscope operating at 2 kV accelerating voltage. Samples were imaged without any additional conductive film.

Fourier transform infrared spectroscopy (FTIR) spectra were measured in the range of 400–4000 cm^{-1} on a Perkin Elmer FT-IR System infrared spectrometer using KBr pellets (1 mg of the substance was mixed with 200 mg KBr and these pellets were pressed in vacuum atmosphere).

The amount of electrodeposits was evaluated by gravimetric method using ABJ 220-4M (Kern&Sohn GmbH) type balances. The accuracy of the method was 0.0001 g.

3. Results and discussion

3.1. Structure and morphology of as-deposited films

The composition and structure of the as-deposited films on *AISI 304* stainless steel plates and *Bekipor ST 20AL3* mesh were investigated using X-ray powder diffraction (Fig. 1). XRD analysis indicated patterns characteristic to α -cobalt hydroxide $\text{Co}(\text{OH})_2$ (d -spacing – 0.274, 0.268, 0.237 *etc.* nm; JCPDF 2-925) and cobalt acetate $\text{Co}(\text{CH}_3\text{COO})_2$ (d -spacing – 0.690, 0.479, 0.318 *etc.* nm.; JCPDF 1-110) as for the prepared film [27].

The FTIR spectrum of the prepared film is shown in Fig. 2. Results confirmed that cobalt hydroxide with intercalated acetate and nitrate ions is formed during electrochemical deposition [27].

The large absorption band centered at 3431 cm^{-1} can be assigned to the stretches of hydroxy groups. The peaks at 1578 and 1385 cm^{-1} can be attributed to the stretching COO vibrations of the free acetate ion while

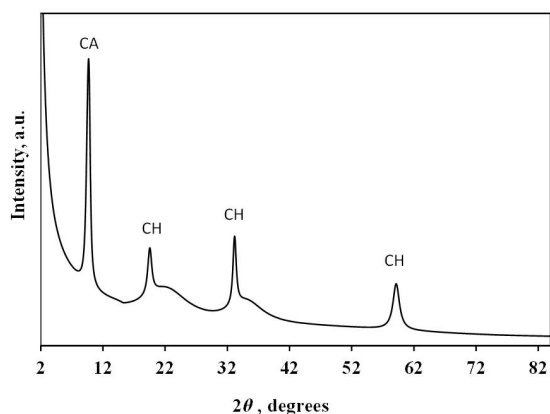


Figure 1. XRD pattern of as-deposited cobalt hydroxide film. Indexes: CA – cobalt acetate, CH – cobalt hydroxide.

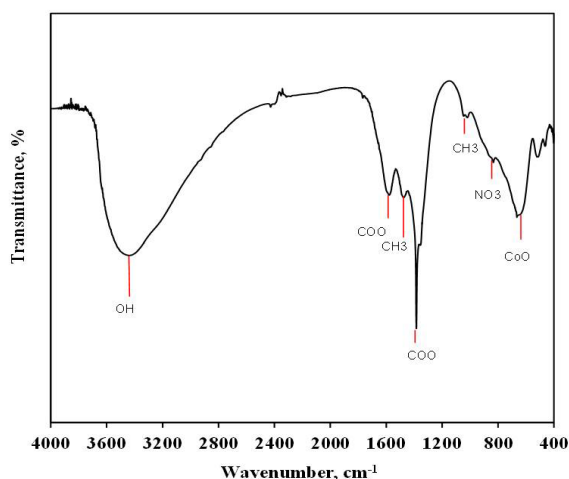


Figure 2. FTIR spectrum of as-deposited cobalt hydroxide.

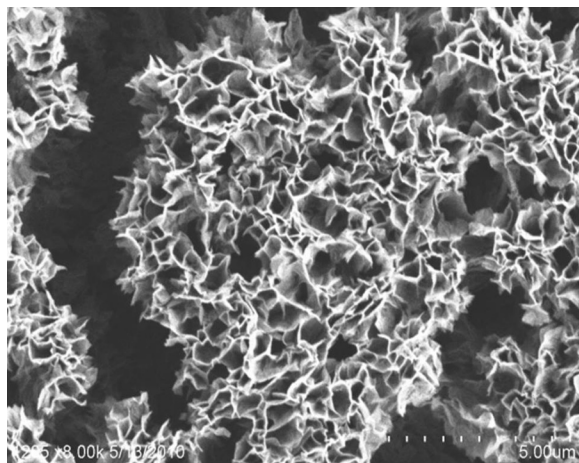


Figure 3. Representative SEM image of as-deposited cobalt hydroxide on AISI 304 stainless steel plate at $\times 8000$ magnification.

NO_3 vibrations are detected at 834 cm^{-1} [20,21,28]. The absorption band at 666 cm^{-1} can be ascribed to Co–OH vibrations. Other peaks at 1474 , 1020 and 458 cm^{-1} show the presence of CH_3 groups.

SEM images of the deposited cobalt hydroxide films on AISI 304 stainless steel are shown in Fig. 3. The distinctive clustering behaviour can be seen at lower magnification while higher magnification revealed a lamellar structure.

As the capacitance of the energy storing system strongly depends on the surface area of active substance, corrosion-resistant *Bekipor ST 20AL3* mesh was used. SEM images of the mesh before the deposition (Fig. 4a) show that this plate is a composition of chaotically situated filaments. Fig. 4c has revealed that after electrochemical deposition the same lamellar cobalt hydroxide structure is formed. Furthermore part *b* of Fig. 4 shows that all filaments are coated separately and no internal area is filled during the deposition.

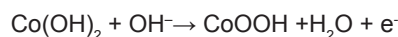
3.2. Capacitive properties of the prepared films on AISI 304 stainless steel

To evaluate the efficiency of supercapacitors, electrochemical measurements of all films were performed. The capacitive behavior of the substance can be evaluated from cyclic voltammetry (CV). The specific capacitance is calculated using the following formula [3]:

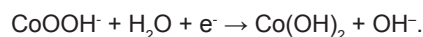
$$SC = \frac{Q}{\Delta E \cdot \Delta m} \quad (1)$$

Here, Q is anodic charge in coulombs, ΔE is a potential range in volts and Δm is the active substance mass in grams.

Fig. 5 shows the cyclic voltammetric curves of the deposited $\text{Co}(\text{OH})_2$ films on the AISI 304 type stainless steel at various amounts of active substance. Several characteristic peaks and the reversibility of a process were registered in the cyclic voltammograms. The anodic peak A_1 around -0.1 V may be related to cobalt hydroxide oxidation into oxyhydroxide form [4]:



Cathodic peak K_1 corresponds to reversible process:



According to the results showed in Table 1 and Fig. 5 the highest value of specific capacitance (490 F g^{-1}) is reached when the mass of active substance is $13 \times 10^{-4} \text{ g}$. It was determined that capacitive properties

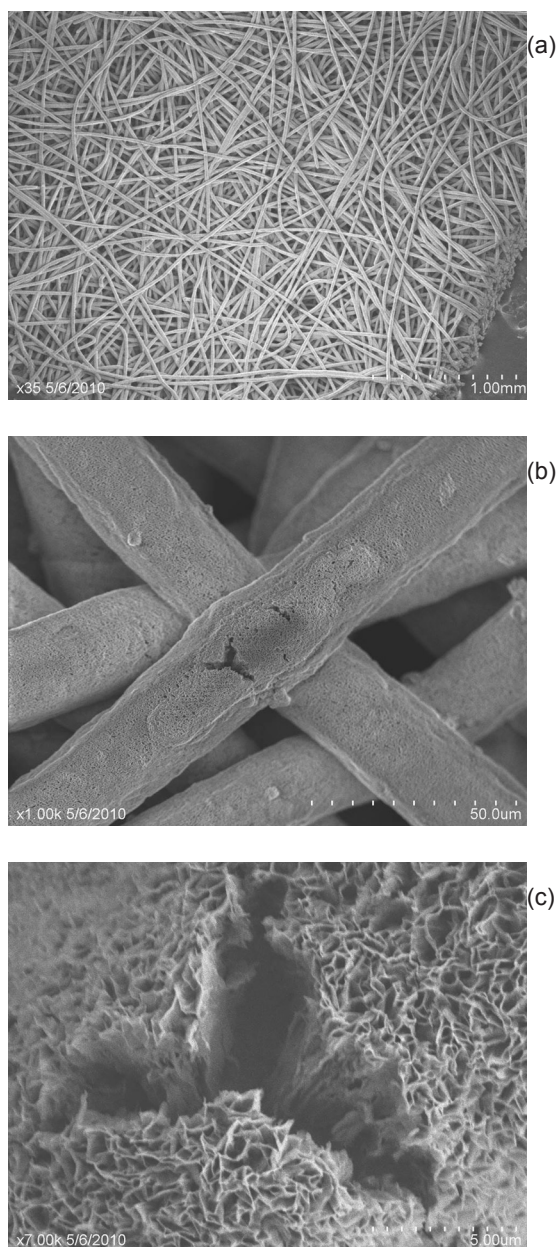


Figure 4. Representative SEM images of as-deposited cobalt hydroxide on Bekipor ST 20AL3 mesh at various magnifications: a – $\times 35$; b – $\times 1000$; c – $\times 3000$.

and values of specific capacitance decreases with the increasing mass of active substance.

Cobalt(II,III) oxide is known for high redox activity and great reversibility [29]. In this work the measurements of a specific capacitance were performed with cobalt oxide films Co_3O_4 on *AISI 304* stainless steel plates. The films were prepared by heating cobalt hydroxide films at 673 K temperature for 3 hours. The formation of cobalt oxide Co_3O_4 was confirmed in the previous work by X-ray powder diffraction (XRD), Fourier transform

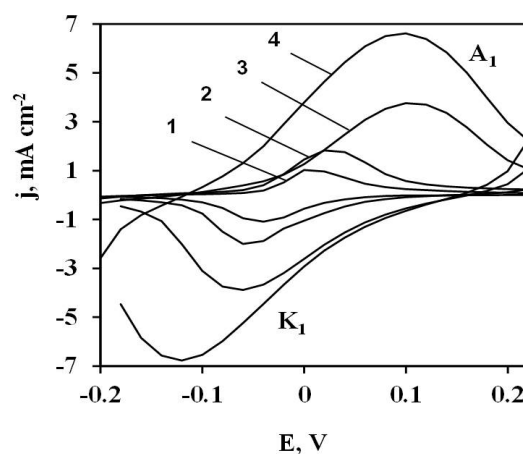


Figure 5. Cyclic voltammograms of $\text{Co}(\text{OH})_2$ films on *AISI 304* type steel in 0.1 M NaOH solution with the different active substance mass in grams: 1 – 2×10^{-4} ; 2 – 3×10^{-4} ; 3 – 8×10^{-4} ; 4 – 13×10^{-4} . Potential scan rate 20 mV s^{-1} .

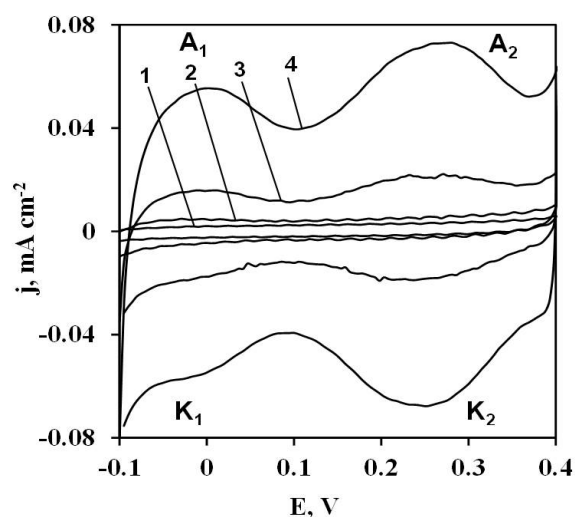
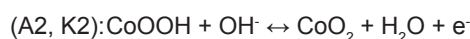
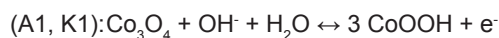


Figure 6. Cyclic voltammograms of Co_3O_4 films on *AISI 304* type steel in 0.1 M NaOH solution with the different active substance mass in grams: 1 – 3×10^{-4} ; 2 – 4×10^{-4} ; 3 – 7×10^{-4} ; 4 – 14×10^{-4} . Potential scan rate 20 mV s^{-1} .

infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) [27].

Cyclic voltammograms of annealed cobalt oxide Co_3O_4 film are shown in Fig. 6. Several characteristic peaks were registered, which correspond to the conversion between different cobalt oxidation states [29]:



Unfortunately the evaluation of specific capacitance displayed relatively low capacitance (Table 2). According

Table 1. Capacitive characteristics of $\text{Co}(\text{OH})_2$ films on *AISI 304* type stainless steel.

Duration of synthesis, min	Mass of active substance, g	Potential range, V	Electric charge, C	Specific capacitance, F g^{-1}
1	0.0003	0.4	0.011	92
5	0.0008		0.13	406
10	0.0013		0.255	490
12	0.0015		0.21	350

Table 2. Capacitive characteristics of Co_3O_4 films on *AISI 304* mesh.

Duration of synthesis, min	Mass of active substance, g	Potential range, V	Electric charge, C	Specific capacitance, F g^{-1}
1	0.0003	0.6	0.00035	2
2	0.0004	0.6	0.00100	4
5	0.0007	0.5	0.00160	5
10	0.0014	0.5	0.00532	8

Table 3. Capacitive characteristics of $\text{Co}(\text{OH})_2$ films on *Bekipor ST 20AL3* mesh.

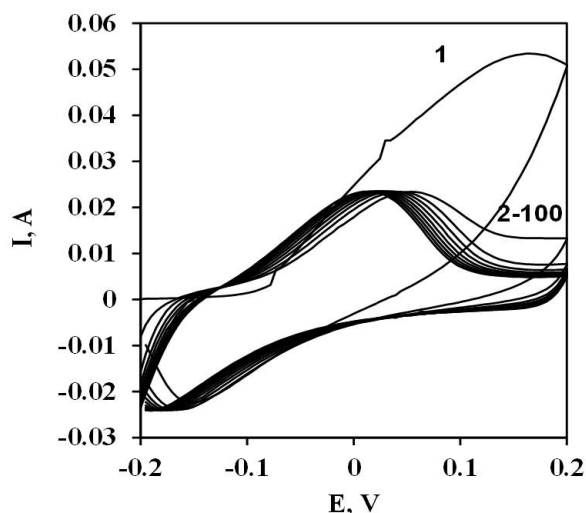
Duration of synthesis, min	Mass of active substance, g	Potential range, V	Electric charge, C	Specific capacitance, F g^{-1}
1	0.0004	0.4	0.038	238
4	0.0005		0.193	965
5	0.0007	0.3	0.193	689
6	0.0008		0.037	154

to these results temperature treatment has a detrimental effect on the specific capacitance of prepared films. No further measurements using cobalt oxide Co_3O_4 films were performed.

3.3. Capacitive properties of prepared coatings on *Bekipor ST 20AL3* mesh

The electrochemical measurements were performed with cobalt hydroxide films on the *Bekipor ST 20AL3* mesh deposited under the same conditions as on *AISI 304* plates. The measurements of specific capacitance were performed using cyclic voltammetry. Fig. 7 shows the CV curves for multicyclic process where great stability of the film is observed.

The relation between specific capacitance and mass of active substance was investigated. It was determined that a limiting value exists, from which specific capacitance decreases with the increasing mass of active substance (Table 3). When optimal mass of active substance is reached, the growth of film layers


Figure 7. Cyclic voltammograms of $\text{Co}(\text{OH})_2$ films on *Bekipor ST 20AL3* mesh in 0.1 mol L^{-1} NaOH solution. The potential scan rate is 20 mV s^{-1} , mass of deposited $\text{Co}(\text{OH})_2$ is $5 \times 10^{-4} \text{ g}$.

begins. This leads to the decrease of surface area and specific capacitance.

It was calculated that the best values of specific capacitance are reached when the duration of synthesis is 4 minutes and mass of active substance is 5×10^{-4} g.

4. Conclusions

In this work cobalt oxide films were deposited on *AISI 304* type stainless steel and *Bekipor ST 20AL3* stainless steel meshes. The deposition was carried out under galvanostatic conditions using 0.05 M $\text{Co}(\text{CH}_3\text{COO})_2$ + 0.1 M KNO_3 solution. The structure and morphology of obtained films were studied by scanning electron

microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). It was determined that the deposited films consist mainly of α -cobalt hydroxide with acetate ions intercalated into the interlayer region. Capacitive properties of the films were investigated by cyclic voltammetry (CV). The highest specific capacitance was estimated to be 945 F g^{-1} for $\text{Co}(\text{OH})_2$ film on *Bekipor ST 20AL3* mesh.

Acknowledgements

The authors gratefully acknowledge Professor L. Kiwi-Minsker (Institute of Chemical Engineering, EPFL, Switzerland) for the kind donation of MFF samples.

References

- [1] C.D. Lokhande, D.P. Dubal, O.S. Joo, *Curr. Appl. Phys.* 11, 255 (2011)
- [2] H. Chen, T.N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, *Prog. Nat. Sci.* 19, 291 (2009)
- [3] V. Gupta, T. Kusahara, H. Toyama, S. Gupta, N. Miura, *Electrochem. Commun.* 9, 2315 (2007)
- [4] C. Yuan, X. Zhang, B. Gao, J. Li, *Mat. Chem. Phys.* 101, 148 (2007)
- [5] P. Oliva, J. Leonardi, J.F. Laurent, C. Delmas, J.J. Braconnier, M. Figlarz, F. Fievet, A.D. Guibert, *J. Power Sources* 8, 229 (1982)
- [6] S.L. Chou, J.Z. Wang, H.K. Liu, S.X. Dou, *J. Electrochem. Soc.* 155, A926 (2008)
- [7] W.J. Zhou, M.W. Xu, D.D. Zhao, C.L. Xu, L. Li, *Micropor. Mesopor. Mat.* 117, 55 (2009)
- [8] S.G. Kandalkar, J.L. Gunjekar, C.D. Lokhande, *Appl. Surf. Sci.* 254, 5540 (2008)
- [9] J.K. Chang, C.M. Wu, I.W. Sun, *J. Mat. Chem.* 20, 3729 (2010)
- [10] W.J. Zhou, D.D. Zhao, M.W. Xu, C.L. Xu, H.L. Li, *Electrochim. Acta* 53, 7210 (2008)
- [11] A.D. Jagadale, V.S. Kumbhar, D.S. Dhawale, C.D. Lokhande, *Electrochim. Acta* 98, 32 (2013)
- [12] M. Kundu, L.F. Liu, *J. Power Sources* 243, 676 (2013)
- [13] M.S. Halper, J.C. Ellenbogen, *Supercapacitors: A Brief Overview* (MITRE, McLean, Virginia, 2006)
- [14] L.Y. Gong, X.H. Liu, L.H. Su, L.Q. Wang, *J. Solid State Electr.* 16, 297 (2012)
- [15] Y. Asano, T. Komatsu, K. Murashiro, K. Hoshino, *J. Power Sources* 196, 5215 (2011)
- [16] M. Aghazadeh, *J. Appl. Electrochem.* 42, 89 (2012)
- [17] M.S. Wu, D.S. Chan, K.H. Lin, J.J. Jow, *Mat. Chem. Phys.* 130, 1239 (2011)
- [18] A. Safavi, S.H. Kazemi, H. Kazemi, *Electrochim. Acta* 56, 9191 (2011)
- [19] C.M. Wu, C.Y. Fan, I.W. Sun, W.T. Tsai, J.K. Chang, *J. Power Sources* 196, 7828 (2011)
- [20] M. Rajamathi, P.V. Kamath, R. Seshadri, *Mater. Res. Bull.* 35, 271 (2000)
- [21] Y.C. Zhu, H.L. Li, Y. Kolytyn, A. Gedanken, *J. Mater. Chem.* 12, 729 (2002)
- [22] M. Dixit, G.N. Subbanna, P.V. Kamath, *J. Mater. Chem.* 6, 1429 (1996)
- [23] M. Kurmoo, *Chem. Mater.* 11, 3370 (1999)
- [24] L.F. Liu, *Nanoscale* 5, 11615 (2013)
- [25] L.F. Liu, *J. Power Sources* 239, 24 (2013)
- [26] I. Yuranov, L. Kiwi-Minsker, A. Renken, *Appl. Catal. B-Environ.* 43, 217 (2003)
- [27] I. Kelpsaite, J. Baltrusaitis, E. Valatka, *Mater. Sci.-Medz.* 17, 236 (2011)
- [28] Y.P. Yang, R.S. Liu, K.L. Huang, L.P. Wang, S.Q. Liu, W.W. Zeng, *T. Nonferr. Metal. Soc.* 17, 1334 (2007)
- [29] Y. Gao, S. Chen, D. Cao, G. Wang, J. Yin, *J. Power Sources* 195, 1757 (2010)