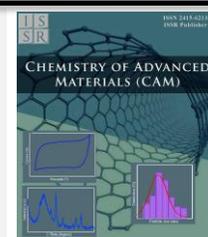


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Original paper

Cobalt Oxide Supercapacitor Electrode Recovered from Spent Lithium-Ion Battery

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Abstract

In this study, cobalt oxide from spent lithium-ion batteries has been successfully recovered using the electrodeposition process. XRD showed the formation of Co₃O₄ phase and XPS showed two significant peaks of Co₃O₄ correlated to Co 2p_{1/2} and Co 2p_{3/2} and a significant peak which is related to Co₃O₄ correlated to O 1S. FTIR spectra showed two stretching bands Co(III)-O and Co(II)-O confirms the material composition of Co₃O₄. The electrodeposited material showed porous sheets-like morphology. The specific capacitance was found to be 143 F/g at a current density of 0.5 A/g.

1. Introduction

An advanced version of capacitors, scientists innovates supercapacitors with a unique ability to combine energy storage capabilities which promising energy storage with high-power densities and long cyclic stability. In 1957, electrochemical capacitor patent was given and the first appearance in the market was in 1969 [1, 2].

Recently, a lot of efforts are put in the research to fulfill the requirements of the recent technology which need a high capacity and power density supercapacitor. The key component of a supercapacitor is the electrode material which controls the main parameters of supercapacitor such as specific capacitance, cycling stability, and power density [3]. There are two types of the

supercapacitor. Firstly, electrical double-layer supercapacitors that have no chemical reaction during the charging and discharging processes. However, only the dielectric capacitance which is mainly proportional to the surface area of the electrode [4-6]. Secondly, the pseudocapacitors (faradic supercapacitors) which have a reversible redox reaction, similarly to the redox reaction occurring in the batteries [7]. Pseudocapacitors depend on the charge transfer between the electrode and the electrolyte through a fast redox reaction. Metal oxides are examples of pseudocapacitors which can store the charges during charging and discharging processes [4, 8].

The scientific research pays attention to the pseudocapacitors because it has a specific capacitance that is higher than the electrodouble layer capacitance [9]. The pseudocapacitor electrodes include metal oxides, metal hydroxides, and conducting polymers [10-12]. Particularly, transition metal oxides (TMO) are preferred among the electrodes materials due to its higher power output, low internal resistance, and multiple oxidation states which contribute to the high specific capacitance in a device [13]. Among TMO, cobalt oxide characterizes of high theoretical specific capacitance 3560 F/g, low cost, and great redox activity which leads scientific researchers to do a lot of efforts to improve the practical capacitance to reach the theoretical value [14-17]. Furthermore, recent researches have obtained high values of specific capacitance of cobalt oxide on the account of its morphology and size for instance: ultrathin nanosheets, nanocubes, microsphere, nanobox and well-defined hierarchical nanostructures [14, 15, 18-20].

In addition to the incredible properties and performances of cobalt oxide, it has a high statistical economic cost drawback. Cobalt oxide price increased from 20 to 59 US\$ Kg⁻¹ in 1998 and

2017 respectively [21, 22]. Therefore, looking for a low-cost production method is needed. Presently, the possession of electronic gadgets has transformed from human luxury to basic human needs. Following the exponential increase in electronic gadget demand, the production of lithium-ion battery (LiB) should be expanded. Yet, LiB is still the most widely used energy storage devices in electronic gadget [23, 24]. The disposal of LiB in electronic gadget is unavoidable due to the finite cycle life of LiB. In this context, the disposal of LiB could cause tremendous environmental disaster, if it is not properly handled because of the contained toxic chemicals and heavy metals such as cobalt [25]. Furthermore, it would be a mistake from the economical point of view if the heavy metals are not recovered before LiB disposal.

Many approaches were done to recover cobalt from spent lithium-ion batteries such as acid leaching, solvent extraction, bioleaching, Chemical precipitation and electrochemical recovery [26] which could extract more than 99% yield of the cobalt from the battery [26-28]. On the other hand, LiB should be more positiveness recycling by connecting the recovered material and the real application. Few studies reported the specific capacitance of cobalt oxide recovered from LiB [21, 29, 30].

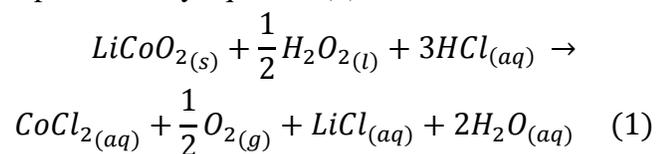
In this context, the electrochemical recovery of cobalt oxide was reported. The prepared material was characterized by different techniques and evaluated as supercapacitor electrodes.

2. Materials and Methods

2.1 Leaching solution preparation

Discharge Samsung 3.7 V LiB was physically dismantled and separated. Cathode powder was dried at 80 °C for 24 h followed by washing in warm water under agitation to remove

the organic solvents then dried in air at 80 °C the dried powder (10 g) was dissolved in the leaching solution (470 mL of 3 M HCl and 30 mL of H₂O₂) and then stirred at 80 °C for 2 h. The pH of the solution was adjusted to 5 using NaOH solution. The leaching chemical reaction could be represented by equation (1):



2.2 Cobalt oxide electrodeposition

Cobalt oxide was prepared as a thin film on Ni foam by electrodeposition from the leaching solution. The process was performed using chronoamperometry under a constant voltage of -1 V applied AUTOLAB potentiostat/galvanostat; PGSTAT101 through three electrode system for 50 s. Three electrodes are Ni foam as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode.

2.3 Characterization techniques

The phase of the prepared materials was investigated using a Rigaku Miniflex II X-ray diffractometer, Japan equipped with an automatic divergent slit. Diffraction patterns were obtained using Cu-K α radiation ($\lambda = 0.15418$ nm) and a graphite monochromator. The chemical bonds were examined using a Perkin Elmer Spectrum 100 spectrophotometer, the USA over the range of 400-4000 cm⁻¹. Morphology of the materials was analyzed using a JEOL JSM-7800 F, FESEM, USA field emission scanning electron microscope operating at 30.0 kV. The oxidation state of cobalt was studied by an Ulvac-Phi/Phi 5000 Versaprobe II spectrometer, XPS, Japan X-ray photoelectron spectrometer.

Electrochemical studies were performed in the three-electrode system, by an AUTOLAB

PGSTAT101 potentiostat/galvanostat with frequency response analyzer. Cyclic voltammetry (CV), Galvanostatic charge/discharge (CD) tests were performed in the potential range between 0 and 0.4 V vs. Ag/AgCl in 5 M KOH.

3. Results and Discussion

3.1 Structural analysis

XRD patterns for the electrodeposited electrode (Fig. 1) shows diffraction peaks at 2 θ of 10°, 37.3° and 66.5° correspond to the (1 1 1), (3 1 1) and (4 4 0) planes which related to Co₃O₄ phase (COD, 9005887) [31]. Moreover, the XRD data does not show any other peak which gives a confirmation that the electrochemical technique of recovering cobalt oxide from spent LiB has high purity.

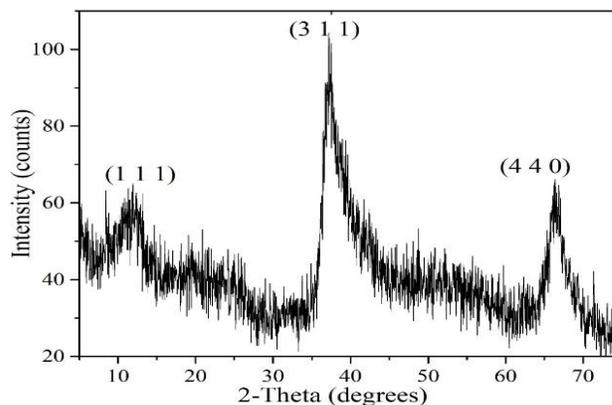


Figure 1: XRD patterns of recovered cobalt oxide.

In order to emphasize the chemical composition, X-ray photoelectron spectroscopy (XPS) analysis was performed. Fig. 2(a) shows two characteristic significant peaks of Co₃O₄ with a binding energy of 780 and 795.2 eV correlated to Co 2p_{1/2} and Co 2p_{3/2} with orbital splitting energy of 15.2 eV and both of them demonstrate the existence of Co⁺² and Co⁺³ [32, 33]. In addition, O 1s XPS spectrum in Fig. 2(b) represents a significant peak at 530 eV which is related to Co₃O₄. Another peak related to a hydroxyl group in

or on water between the deposition material and nickel foam with a binding energy of 530.9 eV.

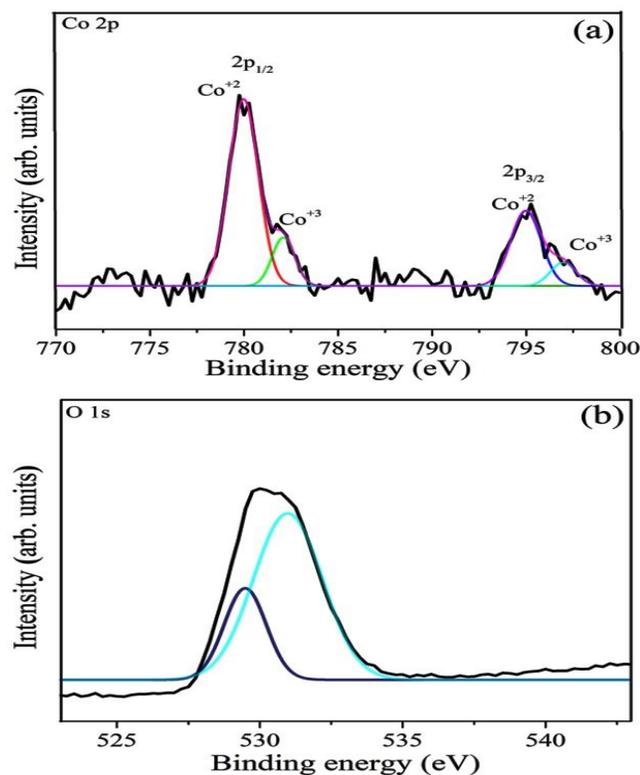


Figure 2: XPS spectra of Co 2p (a) and O 1s (b) of recovered cobalt oxide.

FTIR spectra of the electrodeposited sample in Fig. 3. show four bands, two absorption bands at 3347 and 1640 cm^{-1} which belong to absorbed water molecules. Moreover, there are two particular bands produced from the stretching vibrations of the cobalt-oxygen bond. The first one is at 680 cm^{-1} and results of the vibrations of Co(III)-O bonds. Also, the second one is at 558 cm^{-1} and related to Co-O stretching [34, 35]. The characteristic bands support the formation of Co_3O_4 phase as claimed in XRD analysis.

3.2 Morphological analysis

FESEM images of material are shown in Fig. 4. The surface morphology clearly shows a sheet-like morphology as shown in Fig. 4(a). Whereas in Fig. 6(b). The sheets have a mean thickness of 13

nm. The obtained morphology is quite close to those obtained in hydrothermal synthesis [36]. This porous sheet-like structure is highly preferred for ion penetration and charge accumulation in the electrochemical application, as it is discussed in the next sections. Moreover, the surface morphology shows much porosity than the previous studies cobalt from spent LiB [21, 22, 30].

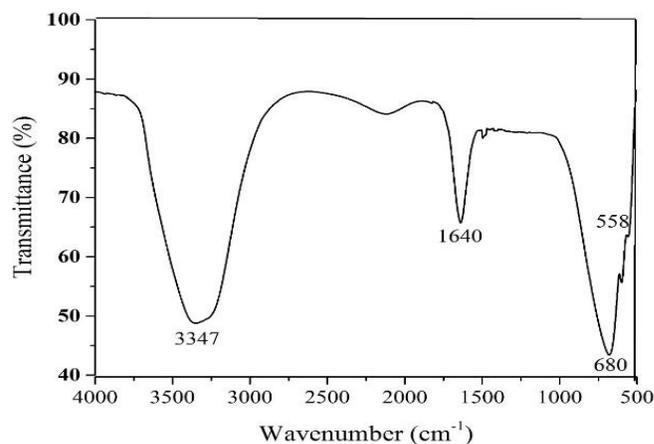


Figure 3: FTIR spectrum of recovered cobalt oxide.

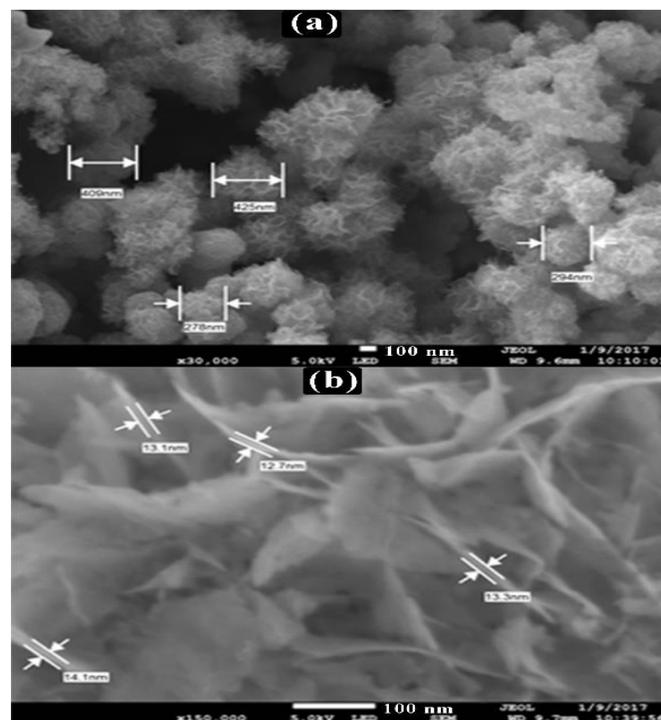
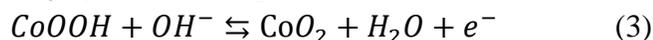
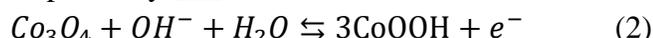


Figure 4: FESEM images of recovered cobalt oxide at (a) 30 kx and (b) 150 kx magnifications.

3.3 Electrochemical studies

Fig. 5(a) shows the cyclic voltammograms of cobalt oxide electrode. Moreover, the cyclic voltammogram at 1 mV/s as shown in the inset, demonstrates two reversible redox peaks (O1/R1) and (O2/R2) which correlated to $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ represented by equations (2) and (3) respectively [13].



Furthermore, Specific capacitance (C_{CV}) was calculated from cyclic voltammograms using the following equation [7]:

$$C_{CV} = \frac{\int I dV}{2 \nu m \Delta V} \quad (4)$$

Where I is the current, ΔV is the potential window, ν is the scan rate and m is the active material mass. As shown in Fig. 5(b), the specific capacitance is found to be maximum of 87 F/g at a scan rate of 1 mV/s and a minimum of 53 F/g at a scan rate of 100 mV/s. The results of the current study are higher than the findings reported in previous studies (13 and 31 F/g at 1 mV/s) [29, 30]. The high results found are due to the sheets-like morphology of cobalt oxide electrode which gives smaller particle and grain size and more porosity than the previous reports.

Galvanostatic charge/discharge curves for cobalt oxide electrode at different current densities from 0.5 to 5 A/g displayed in Fig. 6(a) which indicate the suitability of the electrode in supercapacitor applications. Moreover, Fig. 6(a) at a current density of 0.5 A/g reveals two regions in the discharge curves. Firstly, the slope variation which starts from 0.4 V to 0.11 V (72%). Secondly, the linear slope start from 0.11 V to 0 V is (28%). The slope variation in the discharge curve corresponding to the pseudocapacitance that has more percentage. This positive correlation found confirms FESEM images that the deposited electrode has more active ions due to the porosity

which enhances specific capacitance by pseudocapacitance effect [13]. Furthermore, the specific capacitance (C_{CD}) was calculated in all of the current densities ranges as shown in Fig. 6(b). from discharge curves using the following equation [7]:

$$C_{CD} = \frac{I t_d}{V m} \quad (5)$$

Where t_d is the discharge time and V is the operating voltage. C_{CD} was found to be 143 F/g at 0.5 A/g [37].

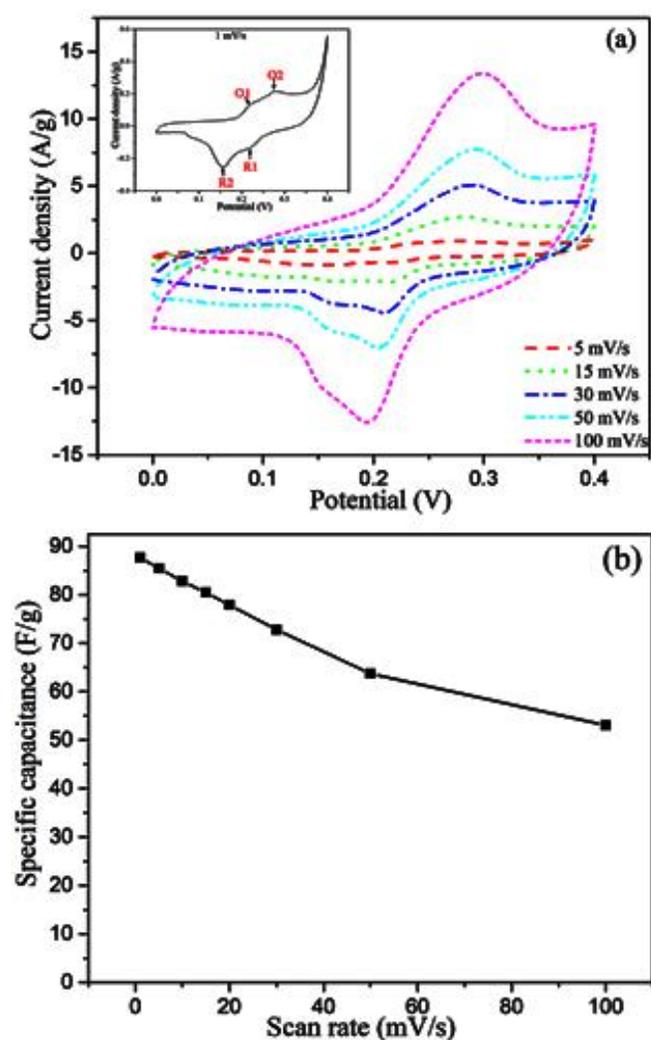


Figure 5: Cyclic voltammetry curves at different scan rates (inset is the cyclic voltammetry curve at 1 mV/s) (a) and specific capacitance versus scan rate (b) of cobalt oxide electrode.

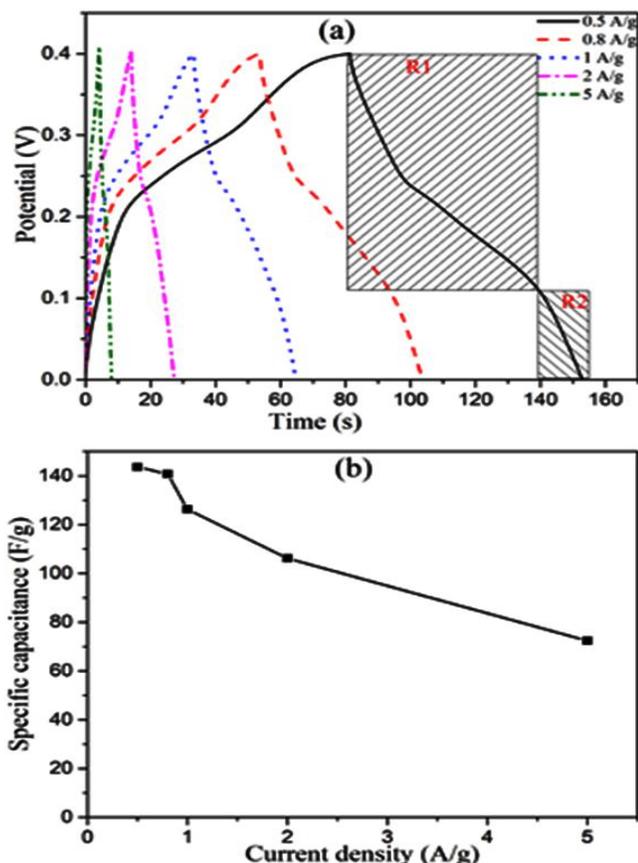


Figure 6: Galvanostatic charge/discharge curves at different current densities (a) and specific capacitance as a function of discharge current density (b) of cobalt oxide electrode.

4. Conclusions

Cobalt oxide is successfully recovered from LiB. XRD shows three peaks related to Co_3O_4 structure. XPS and FTIR confirm the binding energy and the bonding related to Co_3O_4 . FESEM images indicate sheets-like with a mean thickness of 13 nm. Moreover, cyclic voltammetry and galvanostatic charge/discharge measurements show a specific capacitance of 87 F/g at a scan rate of 1 mV/s and 143 F/g at a current density of 0.5 A/g, respectively.

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References

- [1] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochimica Acta* **45**(15) (2000) 2483-2498.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nature Materials* **7**(11) (2008) 845-854.
- [3] L. L. Zhang, X. S. Zhao, Carbon-based materials as supercapacitor electrodes, *Chemical Society Reviews* **38**(9) (2009) 2520-2531.
- [4] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chemical Society Reviews* **41**(2) (2012) 797-828.
- [5] G. A. M. Ali, S. A. Makhlof, M. M. Yusoff, K. F. Chong, Structural and electrochemical characteristics of graphene nanosheets as supercapacitor electrodes, *Reviews on Advanced Materials Science* **40**(1) (2015) 35-43.
- [6] G. A. M. Ali, S. A. A. Manaf, D. A. K. F. Chong, G. Hegde, Superior supercapacitive performance in porous nanocarbons, *Journal of Energy Chemistry* **25**(4) (2016) 734-739.
- [7] S. G. Krishnan, M. H. A. Rahim, R. Jose, Synthesis and characterization of MnCo_2O_4 cuboidal microcrystals as a high performance pseudocapacitor electrode, *Journal of Alloys and Compounds* **656** (2016) 707-713.
- [8] B. Babakhani, D. G. Ivey, Improved capacitive behavior of electrochemically synthesized Mn oxide/PEDOT electrodes utilized as electrochemical capacitors, *Electrochimica Acta* **55**(12) (2010) 4014-4024.
- [9] F. Shi, L. Li, X.-l. Wang, C.-d. Gu, J.-p. Tu, Metal oxide/hydroxide-based materials for supercapacitors, *RSC Advances* **4**(79) (2014) 41910-41921.
- [10] G. A. M. Ali, M. M. Yusoff, Y. H. Ng, N. H. Lim, K. F. Chong, Potentiostatic and

- galvanostatic electrodeposition of MnO₂ for supercapacitors application: A comparison study, *Current Applied Physics* **15**(10) (2015) 1143–1147.
- [11] G. A. M. Ali, O. A. G. Wahba, A. M. Hassan, O. A. Fouad, K. F. Chong, Calcium-based nanosized mixed metal oxides for supercapacitor application, *Ceramics International* **41**(6) (2015) 8230-8234.
- [12] G. A. M. Ali, L. L. Tan, R. Jose, M. M. Yusoff, K. F. Chong, Electrochemical performance studies of MnO₂ nanoflowers recovered from spent battery, *Materials Research Bulletin* **60** (2014) 5-9.
- [13] G. A. M. Ali, O. A. Fouad, S. A. Makhlof, M. M. Yusoff, K. F. Chong, Co₃O₄/SiO₂ nanocomposites for supercapacitor application, *Journal of Solid State Electrochemistry* **18**(9) (2014) 2505-2512.
- [14] M. Pal, R. Rakshit, A. K. Singh, K. Mandal, Ultra high supercapacitance of ultra small Co₃O₄ nanocubes, *Energy* **103** (2016) 481-486.
- [15] M. Cheng, S. Duan, H. Fan, X. Su, Y. Cui, R. Wang, Core@shell CoO@Co₃O₄ nanocrystals assembling mesoporous microspheres for high performance asymmetric supercapacitors, *Chemical Engineering Journal* **327** (2017) 100-108.
- [16] G. A. M. Ali, O. A. Fouad, S. A. Makhlof, M. M. Yusoff, K. F. Chong, Optical and electrochemical properties of Co₃O₄/SiO₂ nanocomposite, *Advanced Materials Research* **1133** (2016) 447-451.
- [17] Q. Yang, Z. Lu, X. Sun, J. Liu, Ultrathin Co₃O₄ nanosheet arrays with high supercapacitive performance, **3** (2013) 3537.
- [18] X. Yan, L. Tian, M. He, X. Chen, Three-dimensional crystalline/amorphous Co/Co₃O₄ Core/Shell nanosheets as efficient electrocatalysts for the Hydrogen evolution reaction, *Nano Letters* **15**(9) (2015) 6015-6021.
- [19] H.-W. Shim, A.-H. Lim, J.-C. Kim, E. Jang, S.-D. Seo, G.-H. Lee, T. D. Kim, D.-W. Kim, Scalable one-pot bacteria-templating synthesis route toward hierarchical, porous-Co₃O₄ superstructures for supercapacitor electrodes, **3** (2013) 2325.
- [20] E. A. A. Aboelazm, G. A. M. Ali, H. Algarni, H. Yin, Y. L. Zhong, K. F. Chong, Magnetic electrodeposition of the hierarchical cobalt oxide nanostructure from spent lithium-ion batteries: Its application as a supercapacitor electrode, *The Journal of Physical Chemistry C* (2018) **122**(23) 12200–12206.
- [21] E. M. Garcia, H. A. Tarôco, T. Matencio, R. Z. Domingues, J. A. F. dos Santos, R. V. Ferreira, E. Lorençon, D. Q. Lima, M. B. J. G. de Freitas, Electrochemical recycling of cobalt from spent cathodes of lithium-ion batteries: its application as supercapacitor, *Journal of Applied Electrochemistry* **42**(6) (2012) 361-366.
- [22] M. B. J. G. Freitas, E. M. Garcia, Electrochemical recycling of cobalt from cathodes of spent lithium-ion batteries, *Journal of Power Sources* **171**(2) (2007) 953-959.
- [23] J. Hu, J. Zhang, H. Li, Y. Chen, C. Wang, A promising approach for the recovery of high value-added metals from spent lithium-ion batteries, *Journal of Power Sources* **351** (2017) 192-199.
- [24] J. Xiao, J. Li, Z. Xu, Recycling metals from lithium ion battery by mechanical separation and vacuum metallurgy, *Journal of Hazardous Materials* **338** (2017) 124-131.
- [25] L. Li, J. Ge, R. Chen, F. Wu, S. Chen, X. Zhang, Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries, *Waste Management* **30**(12) (2010) 2615-2621.
- [26] J. Ordoñez, E. J. Gago, A. Girard, Processes and technologies for the recycling and recovery of spent lithium-ion batteries, *Renewable and Sustainable Energy Reviews* **60** (2016) 195-205.

- [27] M. Contestabile, S. Panero, B. Scrosati, A laboratory-scale lithium battery recycling process|This work has been presented as an invited talk at the 4th International Battery Recycling Congress, Hamburg, Germany, 1–3 July, 1998.1, *Journal of Power Sources* **83**(1) (1999) 75-78.
- [28] S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, Advances in the recovering of spent lithium battery compounds, *Journal of Power Sources* **112**(1) (2002) 247-254.
- [29] E. M. S. Barbieri, E. P. C. Lima, M. F. F. Lelis, M. B. J. G. Freitas, Recycling of cobalt from spent Li-ion batteries as β -Co(OH)₂ and the application of Co₃O₄ as a pseudocapacitor, *Journal of Power Sources* **270** (2014) 158-165.
- [30] E. M. S. Barbieri, E. P. C. Lima, S. J. Cantarino, M. F. F. Lelis, M. B. J. G. Freitas, Recycling of spent ion-lithium batteries as cobalt hydroxide, and cobalt oxide films formed under a conductive glass substrate, and their electrochemical properties, *Journal of Power Sources* **269** (2014) 158-163.
- [31] D. D. M. Prabakaran, K. Sadaiyandi, M. Mahendran, S. Sagadevan, Precipitation method and characterization of cobalt oxide nanoparticles, *Applied Physics A* **123**(4) (2017) 264.
- [32] H. Fan, L. Quan, M. Yuan, S. Zhu, K. Wang, Y. Zhong, L. Chang, H. Shao, J. Wang, J. Zhang, C.-n. Cao, Thin Co₃O₄ nanosheet array on 3D porous graphene/nickel foam as a binder-free electrode for high-performance supercapacitors, *Electrochimica Acta* **188** (2016) 222-229.
- [33] J. Yang, F. Wei, Y. Sui, J. Qi, Y. He, Q. Meng, S. Zhang, Co₃O₄ nanocrystals derived from a zeolitic imidazolate framework on Ni foam as high-performance supercapacitor electrode material, *RSC Advances* **6**(66) (2016) 61803-61808.
- [34] O. A. Fouad, S. A. Makhlouf, G. A. M. Ali, A. Y. El-Sayed, Cobalt/silica nanocomposite via thermal calcination-reduction of gel precursors, *Materials Chemistry and Physics* **128**(1–2) (2011) 70-76.
- [35] C.-W. Tang, C.-B. Wang, S.-H. Chien, Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS, *Thermochimica Acta* **473**(1–2) (2008) 68-73.
- [36] Q. Yang, Z. Lu, Z. Chang, W. Zhu, J. Sun, J. Liu, X. Sun, X. Duan, Hierarchical Co₃O₄ nanosheet@nanowire arrays with enhanced pseudocapacitive performance, *RSC Advances* **2**(4) (2012) 1663-1668.
- [37] G. A. M. Ali, M. M. Yusoff, E. R. Shaaban, K. F. Chong, High performance MnO₂ nanoflower supercapacitor electrode by electrochemical recycling of spent batteries, *Ceramics International* **43**(11) (2017) 8440-8448.

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