ELECTROCHEMICAL CHARACTERIZATION OF SUPERCAPACITORS WITH GLASS WOOL SEPARATOR

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To my parents, my wife and daughter

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ABSTRACT

Supercapacitor, also known as ultracapacitor exhibits higher power density, greater rapid charging and discharging rates, and superior life cycle than a rechargeable battery. The major drawback of supercapacitor is its relatively lower energy density. Previous researchers have proved that the specific capacitance of supercapacitor increases with the increment of electrolyte concentration, which contributes to the improvement of its energy density. Commercial separator, such as cellulose paper, is incapable of withstanding high concentration of electrolyte. A corrosive-resistant material, glass wool has been previously introduced as a potential material for the separator. Nonetheless, studies of the electrochemical performance of supercapacitors with glass wool separator under different types of electrolytes with different concentrations are very limited. This thesis aims to electrochemically evaluate glass wool-based supercapacitor under three types of electrolytes; 1 mol/dm^3 sulfuric acid (H_2SO_4), 6 mol/dm^3 potassium hydroxide (KOH) and 1 mol/dm^3 tetraethylammonium tetrafluoroborate ($TEABF_4$) and compare the performance to an identical supercapacitor with cellulose separator. A systematic study on the effect of high concentrated electrolytes coupled with the glass wool separator was also carried out. The electrochemical performance of the constructed supercapacitors was evaluated through cyclic voltammetry, galvanostatic charge-discharge, electrochemical spectroscopy, and cyclability charge-discharge tests using a symmetrical two-electrode test cell. It is found that the glass wool separator has outperformed cellulose in terms of its internal resistance and power density under the acidic, basic, and organic electrolytes. Interestingly, the glass wool-based supercapacitor coupled with high concentrated H_2SO_4 (18 mol/dm^3) electrolyte exhibits 23% increment of specific capacitance and energy density with almost 100% retention throughout 3000 cycles of charge-discharge process as compared to the one with 1 mol/dm^3 H_2SO_4 electrolyte. The optimum concentration for basic electrolyte KOH suggested is 10 mol/dm^3 which gives 5.3% increment in energy density, 13% increments in power density and excellent cyclability compared to that of 6 mol/dm^3 KOH electrolytes. The application of 2.5 mol/dm^3 concentration of $TEABF_4$ improves the energy and power density by 153% and 3821%, respectively compared to 1 mol/dm^3 $TEABF_4$.

ABSTRAK

Superkapasitor, juga dikenali sebagai ultrakapasitor mempamerkan ketumpatan kuasa yang lebih tinggi, kadar pengecasan dan nyahcas yang lebih pantas, dan kitaran hayat yang lebih baik berbanding bateri yang boleh dicas semula. Kekurangan utama superkapasitor adalah ketumpatan tenaga yang agak rendah. Penyelidik sebelum ini telah membuktikan kemuatan spesifik superkapasitor meningkat dengan peningkatan kepekatan elektrolit, yang seterusnya menyumbang kepada peningkatan ketumpatan tenaga. Pemisah yang terdapat dipasaran seperti kertas selulosa tidak mampu bertahan dalam elektrolit berkepekatan tinggi. Bahan tahan hakisan iaitu wul kaca telah diperkenalkan sebelum ini sebagai bahan yang berpotensi sebagai pemisah. Walau bagaimanapun, kajian mengenai prestasi elektrokimia superkapasitor dengan pemisah wul kaca dengan pelbagai jenis elektrolit dengan kepekatan yang berlainan adalah amat terhad. Kajian ini bertujuan untuk menilai secara elektrokimia superkapasitor berasaskan wul kaca dengan tiga jenis elektrolit; 1 mol/dm^3 asid sulfurik (H_2SO_4), 6 mol/dm^3 kalium hidroksida (KOH) dan 1 mol/dm^3 tetraetilammonium tetrafluroborat ($TEABF_4$) dan kemudian membandingkan prestasinya dengan superkapasitor yang sama tetapi dengan pemisah kertas selulosa. Satu kajian yang sistematik mengenai kesan elektrolit berkepekatan tinggi beserta pemisah wul kaca juga dilakukan. Prestasi elektrokimia superkapasitor yang dibina dinilai melalui ujian kitaran voltametri, cas-nyahcas galvanostatik, spektroskopi elektrokimia, dan ujian cas-nyahcas menggunakan sel uji dua elektrod yang simetri. Didapati, pemisah wul kaca telah mengatasi pemisah kertas selulosa dari segi rintangan dalaman dan ketumpatan kuasa menggunakan elektrolit berasid, beralkali, dan jenis organik. Menariknya, superkapasitor yang dibina berasaskan wul kaca dan elektrolit berkepekatan tinggi, H_2SO_4 (18 mol/dm^3) menghasilkan 23% peningkatan kemuatan spesifik dan ketumpatan tenaga dengan hampir 100% pengekalan kemuatan sepanjang 3000 kitaran cas-nyahcas berbanding dengan elektrolit 1 mol/dm^3 H_2SO_4. Kepekatan yang optimun didapati untuk elektrolit alkali KOH adalah 10 mol/dm^3 yang memberikan peningkatan sebanyak 5.3% kepada kepadatan tenaga, 13% ketumpatan kuasa dan kitaran cas-nyahcas yang sangat baik berbanding dengan 6 mol/dm^3 elektrolit. Penggunaan elektrolit 2.5 mol/dm^3 $TEABF_4$ meningkatkan kepadatan tenaga dan kuasa masing-masing sebanyak 153% dan 3821% berbanding 1 mol/dm^3 $TEABF_4$.

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LIST OF ABBREVIATIONS

BET	-	Brunauer-Emmett-Teller
CV	-	Cyclic Voltammetry
CCD	-	Cyclic Charge Discharge
CNT	-	Carbon Nanotube
ESR	-	Equivalent Series Resistance
EDLC	-	Electrical Double Layer Capacitor
EIS	-	Electrochemical Impedance Spectroscopy
GCD	-	Galvanostatic Charge Discharge
H_2SO_4	-	Sulfuric Acid
KOH	-	Potassium Hydroxide
PC	-	Pseudocapacitor
SEM	-	Scanning Electron Microscopy
$TEABF_4$	-	Tetraethylammonium Tetrafluoroborate

LIST OF SYMBOLS

A	-	Area overlap of two plates, in square meters
C	-	Absolute capacitance
C_{dl}	-	Double layer capacitance
C_H	-	Helmholtz capacitance
C_{diff}	-	Diffusion region capacitance
C_s	-	Specific capacitance
$C_{s,cv}$	-	Static specific capacitance measured by cyclic voltammetry
$C_{s,gv}$	-	Static Specific capacitance measured by galvanostatic
C_d	-	Discharge capacitance
$C(\omega)$	-	Complex capacitance
$C'(\omega)$	-	Complex real capacitance
$C''(\omega)$	-	Complex imaginary capacitance
d	-	Separation between the plates, in meters
dv	-	Voltage response
dt	-	Discharge time
E_d	-	Energy density
ε_r	-	Dielectric constant
ε_0	-	Electric constant
f_r	-	Frequency
m	-	Mass of electrode, in gram
m_t	-	Total mass, in gram
I	-	Current
$\emptyset$	-	Phase angle
P_d	-	Power density
Q	-	Charge in coulombs
R_{esr}	-	Internal resistance
τ_r	-	Relaxation time, in second

ΔV	-	Potential window
V	-	Voltage
V_{drop}	-	Voltage drop
ω	-	Angular frequency
$Z(\omega)$	-	Impedance
$Z'(\omega)$	-	Real impedance
$Z''(\omega)$	-	Imaginary Impedance
$\lvert Z(\omega)\rvert$	-	Impedance vector
π	-	Pi

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Electrical energy storage devices have been playing an increasingly essential role in many rapidly growth application such as in electric vehicles and portable consumer electronics. Besides rechargeable battery, supercapacitor has been recognized as important and promising device for the energy storage purpose [1]. Compared to a conventional dielectric capacitor, supercapacitor possesses an extremely high capacitance and is capable of storing electrical charges up to 10^6 Farad [2]. Owing to its advantages of high power density, long life cycle, and economical, supercapacitor bridges the gap between conventional capacitor and rechargeable batteries.

Depending on the energy storage mechanism, supercapacitor can be categorized into three categories; non-faradic supercapacitor called electric double-layer capacitor (EDLC), faradaic supercapacitor known as pseudocapacitor, and hybrid supercapacitor. An EDLC stores electrical charges electrostatically at the interface layer of electrolyte-electrode and creates a double-layer capacitance effect within the capacitor. Meanwhile, for a pseudocapacitor, the charge-discharge process governs by a reversible Faradaic reduction-oxidation process between the electrode and electrolyte. Unlike rechargeable battery, the reduction-oxidation process in pseudocapacitor is much faster and makes the charging-discharging process relatively quicker than the battery. On the other hand, a hybrid supercapacitor combines both non-faradaic and faradaic charge-discharge mechanisms in a single capacitor [3].

In essence, supercapacitor consists of a pair of active electrodes, separated by a separator that filled with an electrolyte. The active electrode is typically made from activated carbon material. The activated carbon is pre-treated to possess tiny, low volume pores, which consequently increases its surface area for the charges accumulation process.

Besides activated carbon, electrolyte is critical component in supercapacitor construction that determines its operating voltage. The electrolytes can be generally grouped into three categories; aqueous, organic and ionic electrolytes. Both organic and ionic electrolytes possess high potential window of up to 3 V, however both electrolytes suffer from high internal resistance, which affects the power density. Even though the potential window of supercapacitor with an aqueous electrolyte is only limited to 1 V, the electrolyte possesses high ionic conductivity, which reduces the internal resistance of the supercapacitor. In addition, the electrolyte is known to be environment-friendly and inexpensive compared to organic and ionic electrolytes.

In the past decades, many researches have been carried out to improve supercapacitor performance in terms of its power and energy density as well as the cyclability. Beside the operating voltage, energy density is also influenced by the supercapacitor's capacitance, which is significantly depends on the active surface area of the activated electrodes, ions properties and electrolyte concentration. Previous researcher has proven that the increment of concentration of electrolyte significantly increases the specific capacitance of the supercapacitor, but only limited in water bath analysis [4]. Hence, one way to achieve superior power and energy density is by utilizing high concentrated electrolyte coupled with a corrosive-resistant separator. Considering conventional cellulose separator incapable of withstanding high concentrated electrolyte, a corrosive-resistant material, glass wool has been recently introduced as the separator material in supercapacitor application [5]. However, the study was only limited to 1 mol/dm^3 sulfuric acid (H_2SO_4) electrolyte and no further information available particular on high concentrated electrolyte.

Therefore, it is essential to further extend the characterization of supercapacitor containing glass wool as the separator to reveal its performance under different types of high concentrated electrolytes.

1.2 Problem Statement

A corrosive-resistant material, glass wool has been recently introduced as the separator material in supercapacitor application [5]. The glass wool-based supercapacitor outperformed supercapacitors with other separator materials such as cellulose, polypropylene and fiberglass. However, the study is only limited to an aqueous electrolyte of 1 mol/dm^3 H_2SO_4. In addition, very limited reports are available on the performance of the supercapacitor with high concentrated electrolyte that claimed to own superior power and energy capacities. This research aims to systematically evaluate the electrochemical properties of glass wool material as the separator in supercapacitor construction under three types of electrolytes, which are acidic, basic and organic electrolytes. With the utilization of the glass wool material, study on the effect of high concentrated electrolytes in supercapacitor construction was also carried out.

1.3 Objectives

The objectives of this research are:

i. To evaluate and compare the electrochemical properties of supercapacitor with glass wool separator to that of cellulose separator under acidic, basic and organic electrolytes.

ii. To investigate the electrochemical performance of the glass wool-based supercapacitor under high concentration of acidic, basic and organic electrolytes.

1.4 Scope of the Research

The scopes of the research incorporated as follow:

i. The utilization of acidic, basic and organic electrolytes of H_2SO_4, potassium hydroxide (KOH) and tetraethylammonium tetrafluoroborate ($TEABF_4$), respectively as the electrolytes in supercapacitor construction.

ii. The construction of supercapacitor with a symmetrical two-electrode system test cell for all electrochemical evaluation.

iii. The evaluation of the electrochemical properties based on cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), cyclability, and electrochemical impedance spectroscopy (EIS) tests using an electrochemical measuring instrument of Gamry Interface 1000.

iv. The cyclability charge-discharge test is up to 3000 cycles with the applied current that depends on the individual capacity based on GCD test.

1.5 Significance of the Research

Even though the glass wool material is known to be corrosive-resistant material, however its application in supercapacitor containing high concentrated electrolyte is yet to be reported in the past. This research provides beneficial information to researchers in developing superior supercapacitor in term of its power and energy density. The implementation of glass wool separator enables the utilization of high concentrated electrolytes, which consequently leads to higher-rating supercapacitor at relatively lower cost compared to organic solution-based capacitor.

REFERENCES

1. Kim, B.K., et al. Electrochemical Supercapacitors for Energy Storage and Conversion. 2015: 1-25.
2. Jayalakshmi, M., Balasubramanian, K. . Simple Capacitors to Supercapacitors - An Overview. *International Journal of Electrochemical Science*, 2008. **3**(11).
3. González, A., et al. Review on supercapacitors: Technologies and materials. *Renewable and Sustainable Energy Reviews*, 2016. **58**: 1189-1206.
4. Pan, Q., et al. Characteristics of electric double layer in different aqueous electrolyte solutions for supercapacitors. *Wuhan University Journal of Natural Sciences*, 2012. **17**(3): 200-204.
5. Noorden, Z.A., S. Sugawara, and S. Matsumoto. Noncorrosive separator materials for electric double layer capacitor. *IEEJ Transactions on Electrical and Electronic Engineering*, 2014. **9**(3): 235-240.
6. Luo, X., et al. Overview of current development in electrical energy storage technologies and the application potential in power system operation. *Applied Energy*, 2015. **137**: 511-536.
7. Zhong, C., et al. A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chem Soc Rev*, 2015. **44**(21): 7484-539.
8. Meyer, R.T., R.A. DeCarlo, and S. Pekarek. Hybrid Model Predictive Power Management of a Battery-Supercapacitor Electric Vehicle. *Asian Journal of Control*, 2016. **18**(1): 150-165.
9. Liu, C., Z.G. Neale, and G. Cao. Understanding electrochemical potentials of cathode materials in rechargeable batteries. *Materials Today*, 2016. **19**(2): 109-123.
10. Meet Gidwani, A.B., Nikhil Rohra. Supercapacitors: the near Future of Batteries. *International Journal of Engineering Inventions*, 2014. **4**(5).

11. Murray, D.B. and J.G. Hayes. Cycle Testing of Supercapacitors for Long-Life Robust Applications. *IEEE Transactions on Power Electronics*, 2015. **30**(5): 2505-2516.

12. Wang, G., L. Zhang, and J. Zhang. A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev*, 2012. **41**(2): 797-828.

13. *Supercapacitors, also known as ultracapacitors*; Available from: <http://www.futureelectronics.com/en/capacitors/super-caps-capacitor.aspx>. [16 July 2017].

14. Vangari, M., T. Pryor, and L. Jiang. Supercapacitors: Review of Materials and Fabrication Methods. *Journal of Energy Engineering*, 2013. **139**(2): 72-79.

15. Zhang, L.L. and X.S. Zhao. Carbon-based materials as supercapacitor electrodes. *Chem Soc Rev*, 2009. **38**(9): 2520-31.

16. Fic, K., et al. Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. *Energy Environ. Sci.*, 2012. **5**(2): 5842-5850.

17. Barzegar, F., et al. Effect of conductive additives to gel electrolytes on activated carbon-based supercapacitors. *AIP Advances*, 2015. **5**(9): 097171.

18. Senthilkumar, S.T., R.K. Selvan, and J.S. Melo. Redox additive/active electrolytes: a novel approach to enhance the performance of supercapacitors. *Journal of Materials Chemistry A*, 2013. **1**(40): 12386.

19. Soneda, Y., et al. Electrochemical behavior of exfoliated carbon fibers in H2SO4 electrolyte with different concentrations. *Journal of Physics and Chemistry of Solids*, 2004. **65**(2-3): 219-222.

20. Devarajan, T., et al. Novel ionic liquid electrolyte for electrochemical double layer capacitors. *Electrochemistry Communications*, 2009. **11**(3): 680-683.

21. Lewandowski, A., et al. Performance of carbon–carbon supercapacitors based on organic, aqueous and ionic liquid electrolytes. *Journal of Power Sources*, 2010. **195**(17): 5814-5819.

22. Sun, X.-Z.Z., Xiong; Huang, Bo; Ma, Yan-Wei. Effects of Separator on the Electrochemical Performance of Electrical Double-Layer Capacitor and Hybrid Battery-Supercapacitor. *Acta Physico-Chimica Sinica*, 2014. **30**(3).

23. Liivand, K., Thomberg, Thomas, Alar Jänes and Enn Lust. Separator Materials Influence on Supercapacitors Performance in Viscous. *ECS Transactions* 2015/02/10. **64**(20).

24. Cao, W., et al. Strategies to optimize lithium-ion supercapacitors achieving high-performance: Cathode configurations, lithium loadings on anode, and types of separator. *Journal of Power Sources*, 2014. **268**: 841-847.
25. *Electronics-tutorials/Ultracapacitor*; Available from: <http://www.electronics-tutorials.ws/capacitor/ultracapacitors.html>. [16 July 2017].
26. Shulga, Y.M., et al. Supercapacitors with graphene oxide separators and reduced graphite oxide electrodes. *Journal of Power Sources*, 2015. **279**: 722-730.
27. Taer, E., et al. Eggs Shell Membrane as Natural Separator for Supercapacitor Applications. *Advanced Materials Research*, 2014. **896**: 66-69.
28. Chen, Q., et al. Effect of different gel electrolytes on graphene-based solid-state supercapacitors. *RSC Adv.*, 2014. **4**(68): 36253-36256.
29. Tarnow, V. Fiber movements and sound attenuation in glass wool. *J. Acoust. Soc. Am*, 1998. **105, 234**.
30. Jeon, C.-K., et al. A Study on Insulation Characteristics of Glass Wool and Mineral Wool Coated with a Polysiloxane Agent. *Advances in Materials Science and Engineering*, 2017. **2017**: 1-6.
31. *Glasswool (Fiberglass Insulation)*. Available from: <http://www.natindco.in/insualting-products/glasswool>. [16 July 2017].
32. Zhang, S. and N. Pan. Supercapacitors Performance Evaluation. *Advanced Energy Materials*, 2015. **5**(6): 1401401.
33. Noorden, Z.A., Sugawara, S., & Matsumoto, S. Glass wool material as alternative separator for higher rating electric double layer capacitor. *ECS Transactions*, 2013. **53**: 43-51.
34. Brownson, D.A.C. and C.E. Banks. in *The Handbook of Graphene Electrochemistry*, *Interpreting Electrochemistry*. 2014, London: Springer London. p. 23-77.
35. Mabbott, G.A. An introduction to cyclic voltammetry. *Journal of Chemical Education*, 1983. **60**(9): 697.
36. Taberna, P.-L. and P. Simon. in *Supercapacitors: Materials, Systems, and Applications*, *Electrochemical Techniques*. 2013: Wiley-VCH Verlag GmbH & Co. KGaA. p. 111-130.

37. Chen, W., R.B. Rakhi, and H.N. Alshareef. Facile synthesis of polyaniline nanotubes using reactive oxide templates for high energy density pseudocapacitors. *Journal of Materials Chemistry A*, 2013. **1**(10): 3315.

38. Zhou, Y., et al. High volumetric electrochemical performance of ultra-high density aligned carbon nanotube supercapacitors with controlled nanomorphology. *Electrochimica Acta*, 2013. **111**: 608-613.

39. Hyacinthe Randriamahazaka, a.K.A. Electromechanical Analysis by Means of Complex Capacitance of Bucky-Gel Actuators Based on Single-Walled Carbon Nanotubes and an Ionic Liquid. *J. Phys. Chem. C*, 2010. **114**: 17982-17988.

40. Donne, S.W. in *Supercapacitors: Materials, Systems, and Applications*, *General Principles of Electrochemistry*. 2013: Wiley-VCH Verlag GmbH & Co. KGaA. p. 1-64.

41. Umashankar, M. and S. Palaniappan. Hybrid composite of nitrogen functionalized graphene–polyaniline electrode for high performance supercapacitor. *RSC Adv.*, 2015. **5**(86): 70675-70681.

42. Kurig, H., A. Jänes, and E. Lust. Electrochemical Characteristics of Carbide-Derived Carbon|1-Ethyl-3-methylimidazolium Tetrafluoroborate Supercapacitor Cells. *Journal of The Electrochemical Society*, 2010. **157**(3): A272.

43. Taberna, P.L., P. Simon, and J.F. Fauvarque. Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon-Carbon Supercapacitors. *Journal of The Electrochemical Society*, 2003. **150**(3): A292.

44. Yoon, S., et al. Complex capacitance analysis on rate capability of electric-double layer capacitor (EDLC) electrodes of different thickness. *Electrochimica Acta*, 2005. **50**(11): 2255-2262.

45. Zhang, X., et al. Effect of aqueous electrolytes on the electrochemical behaviors of supercapacitors based on hierarchically porous carbons. *Journal of Power Sources*, 2012. **216**: 290-296.

46. Dhelipan, M., et al. Activated carbon from orange peels as supercapacitor electrode and catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *Journal of Saudi Chemical Society*, 2017. **21**(4): 487-494.

47. Jingsong Huang, R.Q., Guang Feng, Bobby G. Sumpter, and Vincent Meunie. in *Supercapacitors: Materials, Systems, and Applications*, *Modern Theories of Carbon-Based Electrochemical Capacitors*. 2013: Wiley-VCH Verlag GmbH & Co. KGaA. p. 167.

48. Stoller, M.D. and R.S. Ruoff. Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy & Environmental Science*, 2010. **3**(9): 1294.

49. Frackowiak, E. in *Supercapacitors: Materials, Systems, and Applications Electrode Materials with Pseudocapacitive Properties*, F.c.B.a.E.z.F. ackowiak, Editor. 2013: Wiley-VCH Verlag GmbH & Co. KGaA. p. 207-233.

50. Zeng, J., L. Wei, and X. Guo. Bio-inspired high-performance solid-state supercapacitors with the electrolyte, separator, binder and electrodes entirely from kelp. *Journal of Materials Chemistry A*, 2017. **5**(48): 25282-25292.

51. Yu, H., et al. Using eggshell membrane as a separator in supercapacitor. *Journal of Power Sources*, 2012. **206**: 463-468.

52. Szubzda, B., et al. Polymer membranes as separators for supercapacitors. *Applied Physics A*, 2014. **117**(4): 1801-1809.

53. Dahlan, D., et al. Effect of TiOon Duck Eggshell Membrane as Separators in Supercapacitor Applications. *Materials Science Forum*, 2015. **827**: 151-155.

54. Y. S. Yang, I.-K.Y., S.-H. Hong, and H.-G. Yun. Characteristics of inkjet-printed separators in grapheme-based supercapacitors. *ECS Transactions*, 2014. **64**(8): 135-137.

55. Venkat Srinivasan, J.W.W. Studies on the Capacitance of Nickel Oxide Films-Effect of Heating Temperature and Electrolyte Concentration. *Journal of The Electrochemical Society*, 1999. **147**: 034-2.

56. Weng, T.W., W. Huang, and K.Y. Lee. Improved electrochemical capacitive characteristics by controlling the carbon nanotube morphology and electrolyte solution concentration. *Vacuum*, 2008. **83**(3): 629-632.

57. Tsay, K.-C., L. Zhang, and J. Zhang. Effects of electrode layer composition/thickness and electrolyte concentration on both specific capacitance and energy density of supercapacitor. *Electrochimica Acta*, 2012. **60**: 428-436.

58. Tian, Y.Y., Jing-Wang; Xue, Rong; Yi, Bao-Lian. Influence of Electrolyte Concentration and Temperature on the Capacitance of Activated Carbon. *Acta Physico-Chimica Sinica*, 2011. **27**(2).

59. Liu, W., et al. Effects of concentration and temperature of EMIMBF4/acetonitrile electrolyte on the supercapacitive behavior of graphene nanosheets. *Journal of Materials Chemistry*, 2012. **22**(18): 8853.

60. Su, Y.Z.H.W.S. Effect of electrolyte concentration on the capacitive properties of NiO electrode for supercapacitors. *Journal of Solid State Electrochemistry*, 2016. **20**(1).

61. Redondo, E., E. Goikolea, and R. Mysyk. The decisive role of electrolyte concentration in the performance of aqueous chloride-based carbon/carbon supercapacitors with extended voltage window. *Electrochimica Acta*, 2016. **221**: 177-183.

62. Zhang, L., et al. Fluorine-free ionic liquid based on thiocyanate anion with propylene carbonate as electrolytes for supercapacitors: Effects of concentration and temperature. *Chemical Research in Chinese Universities*, 2017. **33**(5): 779-784.

63. Shulga, Y.M., et al. Graphene oxide films as separators of polyaniline-based supercapacitors. *Journal of Power Sources*, 2014. **245**: 33-36.

64. Torvinen, K., et al. Pigment-cellulose nanofibril composite and its application as a separator-substrate in printed supercapacitors. *Electronic Materials Letters*, 2015. **11**(6): 1040-1047.

65. XingfengWang, R.S.C., Zelang Jian, Zhenyu Xing, and Xiulei Ji. A 1.8 V Aqueous Supercapacitor with a Bipolar Assembly of Ion-ExchangeMembranes as the Separator. *Journal of The Electrochemical Society,*, 2016. **163**(9).

66. Feng, E., et al. Toughened redox-active hydrogel as flexible electrolyte and separator applying supercapacitors with superior performance. *RSC Advances*, 2016. **6**(79): 75896-75904.

67. Na, R., et al. High performance disulfonated poly(arylene ether sulfone)/poly(ethylene oxide) composite membrane used as a novel separator for supercapacitor with neutral electrolyte and activated carbon electrodes. *High Performance Polymers*, 2016. **29**(8): 984-993.

68. Yaacob, M.F.M., Z.A. Noorden, and J.J. Jamian. Electrochemical impedance behavior of glass wool-based supercapacitors with different concentration of

sulfuric acid. *2016 IEEE International Conference on Power and Energy (PECon)*. 28-29 Nov. 2016. 2016. 723-727.

69. Gamry Instruments, I. *Gamry Intruments Interface 1000 operator's manual.* 2015; Available from: <https://www.gamry.com/assets/Uploads/Interface-1000-Operators-Manual2.pdf>. [16 July 2017].
70. Kim, M., I. Oh, and J. Kim. Effects of different electrolytes on the electrochemical and dynamic behavior of electric double layer capacitors based on a porous silicon carbide electrode. *Phys Chem Chem Phys*, 2015. **17**(25): 16367-74.
71. Ali, G.A.M., et al. Potentiostatic and galvanostatic electrodeposition of manganese oxide for supercapacitor application: A comparison study. *Current Applied Physics*, 2015. **15**(10): 1143-1147.
72. Tõnurist, K., et al. Influence of separator properties on electrochemical performance of electrical double-layer capacitors. *Journal of Electroanalytical Chemistry*, 2013. **689**: 8-20.
73. Zhang, S.S. A review on the separators of liquid electrolyte Li-ion batteries. *Journal of Power Sources*, 2007. **164**(1): 351-364.
74. Zolin, L., et al. Aqueous processing of paper separators by filtration dewatering: towards Li-ion paper batteries. *J. Mater. Chem. A*, 2015. **3**(28): 14894-14901.
75. Dang, Y.-Q., et al. Electrochemical and Capacitive Properties of Carbon Dots/Reduced Graphene Oxide Supercapacitors. *Nanomaterials*, 2016. **6**(11): 212.
76. Gallay, H.G.a.R. in *Supercapacitors: Materials, Systems, and Applications, First Edition*, *Supercapacitor Module Sizing and Heat Management under Electric, Thermal, and Aging Constraints*, F.c.B.a.E. Frackowiak, Editor. 2013: Wiley-VCH Verlag GmbH & Co. KGaA. p. 374-375.
77. Lei, Z., et al. A high-energy-density supercapacitor with graphene–CMK-5 as the electrode and ionic liquid as the electrolyte. *Journal of Materials Chemistry A*, 2013. **1**(6): 2313.
78. Mohammad Shiri, H., A. Ehsani, and J. Shabani Shayeh. Synthesis and highly efficient supercapacitor behavior of a novel poly pyrrole/ceramic oxide nanocomposite film. *RSC Adv.*, 2015. **5**(110): 91062-91068.

79. Yang, P., et al. Quantitative Analysis of Charge Storage Process of Tungsten Oxide that Combines Pseudocapacitive and Electrochromic Properties. *The Journal of Physical Chemistry C*, 2015. **119**(29): 16483-16489.
80. Yang, C., et al. Complex Impedance with Transmission Line Model and Complex Capacitance Analysis of Ion Transport and Accumulation in Hierarchical Core-Shell Porous Carbons. *Journal of the Electrochemical Society*, 2013. **160**(4): H271-H278.
81. Shen, P.W., Chao-Yang; Jiang, San; Sun, Xueliang; Zhang, Jiujun. in *Electrochemical Energy: Advanced Materials and Technologies*, *Advanced Technologies for Supercapacitors*. 2015: CRC Press. p. 451-477.
82. Darling, H.E. Conductivity of Sulfuric Acid Solutions. *Journal of Chemical & Engineering Data*, 1964. **9**(3): 421-426.
83. Meng, T., et al. Ionic Liquid-Based Non-Aqueous Electrolytes for Nickel/Metal Hydride Batteries. *Batteries*, 2017. **3**(1): 4.