Journal of Molecular Liquids 294 (2019) 111671

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

PMMA-RTIL electrolyte for high-energy supercapacitors: A comparison of different anions

Shabeeba P. [a,b,*], Mohamed Shahin Thayyil [a], M.P. Pillai [b], Thasneema K.K. [a]

[a] Department of Physics, University of Calicut, Kerala, Calicut, India
[b] Department of Electronics, NIELIT, Calicut, Kerala, India

A R T I C L E I N F O

Article history:
Received 18 April 2019
Received in revised form 24 July 2019
Accepted 31 August 2019
Available online 02 September 2019

Keywords:
Solid electrolytes
RTIL with different anions
Electrochemical studies
Broad band dielectric study
Supercapacitor applications

A B S T R A C T

Polyionic liquids are a significant part of flexible electrochemical supercapacitor due to its high thermal stability, wide voltage window and its cycle stability. A series of ionogel based on $[P_{14666}][DCA]$, $[P_{14666}][NTf_2]$ and $[P_{14666}][Cl]$ entrapped in the PMMA are developed and examined. The impact of changing anion by fixing cation on the electrochemical system is investigated. The physicochemical properties of the supported ionogel electrolytes are investigated using X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy, thermal gravimetric analysis, Raman spectroscopy, broadband dielectric spectra, and FTIR. The electrochemical performance of the solid-state supercapacitors is evaluated using cyclic voltammetry, charge-discharge cycle, and impedance spectra. This comparative study reveals that the tuning of ionic liquids by the anion has a strong influence on the electrochemical system for energy storage applications. In this work among three ionogel, $[_{P14666}][DCA]$ ionogel exhibited a higher specific capacitance of 437.5 F/g, the specific energy of 136 Wh/kg and specific power of 4 kW/kg than other two ionogels.

1. Introduction

Development of high-performance solid-state energy storage devices is of crucial importance due to wide applications in industry such as fuel cells, supercapacitors, and batteries [1]. Among these supercapacitors are more attracted due to their high power delivering capability, long life cycle, easy fabrication, and low maintenance cost. However, the energy density of supercapacitors are somewhat limited as compared to other enhanced properties, therefore the challenge of increasing energy density is attentive in this area of research [2]. This can be done through increasing cell voltage, thus attention has been focused on electrolytes that would have sufficient thermal and electrochemical stability to operate at high voltage and over a range of temperatures.

Nowadays, Ionic liquid electrolytes are the promising electrolytes to enhance the voltage window in many applications because of their interesting properties like high thermal stability, conductivity, non-volatile and tuneable solubility [3]. Currently, a wide variety of IL cations and anions are existed, but in general phosphonium based ILs have shown better thermal stability, cyclic stability, and electrochemical stability, but have not been studied well. The cation-anion interactions also play an important role in electrochemical reactions thus by simply changing the ions, the physicochemical properties can be tuned for specific applications. A particularly interesting sub-set of ionic liquids are those based upon a tetra hexyl phosphonium cation; research into these compounds has often been unkempt in favor of their phosphonium-based counterparts with particular emphasis on the different anions. It has been observed that tetraalkyl phosphonium-based ionic liquids can offer superior physicochemical properties in comparison to their families [4]. Furthermore, there are only a few systematic studies that directly investigate the effect of changing the different anions by keeping the cation constant [5–7]. It has been noted that altering the anions has a noticeable effect on the physicochemical properties of ILs.

The applicability of aqueous electrolytes restricted because of their volatile, flammable and low stability in electrochemical applications. The replacement of aqueous to gel electrolyte could be overcome these problems and hence improve the performance of the electrochemical cell [8]. Based on the research reports available on phosphonium based ILs, it has better thermal, electrical and chemical properties and it could be used as a good electrolyte for electrochemical studies [9]. Hence, in the present study, we have chosen a series of phosphonium based ILs with different anion for preparation of gel electrolytes and to evaluate the effect of anions on electrochemical applications. Until the present time, publications have been available for ionic liquid gel electrolytes but few research on the anionic influence for solid-state electric double layer supercapacitor. Thus, it is a novel

* Corresponding author.
E-mail address: shabeebanawab@gmail.com (S. P.).

https://doi.org/10.1016/j.molliq.2019.111671
0167-7322/

Table 1
Electrochemical results.

Electrode material	Electrolyte	Mass (g)	ESR (Ω)	C_{cell} (F)	C_{sp} (F/g)	E (Wh/kg)	P (kW/kg)
Activated carbon	$[P_{14666}][DCA]$	0.02	1	4.75	437.5	136	4
Activated carbon	$[P_{14666}][NTf_2]$	0.02	2.5	1.5	105	39	1.6
Activated carbon	$[P_{14666}][Cl]$	0.02	1.5	0.7	78	18.19	2.5

the x-intercept at high-frequency region and $R_s + R_{ct}$ is obtained from the low-frequency x-intercept [13]. The R_{ct} is associated with the interface of electrode-electrolyte which is the combination of both ionic and electronic resistance of the materials. The ionic resistance rest on the charge carrier ions and the porosity of electrode materials and the electronic resistance rest on the contact resistance of the electrode and current collector. Here the effect of resistance due to the current collector is negligible because the chosen PCB copper clad current collector having low resistance, hence R_{ct} is principally due to ionic resistance of electrolytes. The supercapacitor with DCA anions shows smaller semicircle which resembles that it has low ionic resistance and Cl anion shows bigger semicircle which means it has some charge transport limitation to the electrode surface. However, all three anions deliver a channel to charge transfer and the DCA has better compatibility with the activated carbon electrode surface. The obtained R_{ct} of Phosphonium IL with three anions, DCA, NTf_2 and Cl R_{ct} can be calculate from the semicircle intercept at x-axis anions are 30 Ω, 69 Ω and 93 Ω respectively. At high-frequency resistance of electrode-electrolyte represented by R_s and in the mid-frequency region provides the combination of EDLC capacitance and charge transfer resistance. The ion diffusion at Warburg region is attributed by the 45° slope at mid-frequency region. The cyclic stability is also an important aspect for practical applications of EDLC capacitor and it is examined up to 1000 cycles. As shown in Fig. 8b all three cells maintain the cyclic stability until 1000 cycles with a small decrease in a few cycles.

To confirm the specific capacitance, the galvanostatic charge-discharge curves of prepared supercapacitors were studied. In Fig. 8c all three anions exhibit almost linear charge-discharge curve with a small voltage drop (iR drop) at the currency density of 5 A/g. The initial voltage drop in the discharge curve is due to the ohmic resistance between electrode and electrolyte. The almost symmetric triangular shape of GCD curve further confirms the double layer capacitive nature of fabricated cells.

The specific capacitance (Csp), energy density E (Wh/kg) and power density, P (W/kg) can be calculated from the GCD curve by using the equation [14],

$$Cg = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

$$E = \frac{1}{2} Cg \times \Delta V^2 \times \frac{1}{3.6} \tag{2}$$

$$P = \frac{E}{\Delta t} \times 3600 \tag{3}$$

where i is the current density, Δt is the discharge time, ΔV is the voltage drop during discharging and R is the equivalent series resistance obtained from IR drop. The obtained specific capacitance of three ionogels with different anions (DCA, NTf_2, and Cl) are 437.5 F/g, 105 F/g and 78 F/g, respectively. The supercapacitor with DCA anion shows higher capacitance, which is good contract with other results. In Fig. 8d shows the working model of fabricated supercapacitors, we have connected a motor fan to our fabricated supercapacitors and it is worth to note that it can drive a motor over a few minutes (Table 1).

4. Conclusions

A series of ionogel based on $[P_{14666}][DCA]$, $[P_{14666}][NTf_2]$ and $[P_{14666}][Cl]$ entrapped in the PMMA are developed and examined. The impact of changing anion by fixing cation on the electrochemical system has been investigated. All three ionogel exhibited wide electrochemical window, cyclic stability, and electrochemical performance. But compared to $[P_{14666}][NTf_2]$ and $[P_{14666}][Cl]$, $[P_{14666}][DCA]$ exhibited excellent specific capacitance, specific energy, specific power of 437.5 F/g, 136 Wh/kg and 4 kW/kg, respectively. The structural and electrochemical results indicated that the tuning of IL by the anion has a strong influence on the electrochemical system for energy storage applications.

Acknowledgments

Authors thankfully acknowledge fruitful discussions with Pramanic (C-MET Trichur, India); PP Pradyumnan, S. Sindhu (University of Calicut). SP gratefully acknowledges the research fellowship from the UGC India. MST acknowledges the KSCSTE (SRS, SARD), UGC-DAE CSR and UGC (MRP) for financial assistance. A portion of the research was performed using the facilities at CeNSE, IISc, Bengaluru, funded by Diety, Govt. of Ind and CSIF, University of Calicut.

References

[1] K. Kim, High operating voltage supercapacitor using PPy/AC composite electrode based on simple dipping method, J. Chem. 2015 (2015) 1–8.
[2] S. Pilathottathil, T. Kannan Kottummal, M.S. Thayyil, P. Mahadevan Perumal, J. Ambichi Purakakath, Inorganic salt grafted ionic liquid gel electrolytes for efficient solid state supercapacitors: electrochemical and dielectric studies, J. Mol. Liq. 264 (2018) 72–79.
[3] L. Timperman, H. Galiano, Sulfonium Bis(trifluorosulfonimide) Plastic Crystal Ionic Liquid as an Electrolyte at Elevated Temperature for High-energy Supercapacitors, 2012https://doi.org/10.1021/jp3012987.
[4] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2084.
[5] A.R. Muchakayala, et al., Development and supercapacitor application of ionic liquid-incorporated gel polymer electrolyte films, J. Ind. Eng. Chem. (2017)https://doi.org/10.1016/j.jiec.2017.10.009.
[6] H. Abe, M. Aono, Impedance Spectroscopic Study on Room Temperature Ionic Liquid-water Mixtures, 2012.
[7] G. Chen, N. Chen, L. Li, Q. Wang, W. Duan, Ionic Liquid Modified Poly(vinyl alcohol) With Improved Thermal Processability and Excellent Electrical Conductivity, 2018https://doi.org/10.1021/acs.iecr.8b00157.
[8] H.T. Jeong, F. Du, Y. Ryeol, Development of Flexible Energy Storage Device by Using Polymer Electrolyte Based on Ionic Liquid, 2017 6057–6061, https://doi.org/10.1002/slct.201701073.
[9] R.K. Blundell, P. Licence, Quaternary Ammonium and Phosphonium Based Ionic Liquids: A Comparison of Common Anions, 2014 15278–15288, https://doi.org/10.1039/c4cp01901f.
[10] M.A. Kareem, F.S. Mjalli, M.A. Hashim, I.M. Alnashef, Phosphonium-based Ionic Liquids Analogues and Their Physical Properties, 2010 4632–4637.
[11] O. Achaw, A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope, 2002.
[12] J. Shu, S. Cheng, H. Xia, L. Zhang, J. Peng, Copper loaded on activated carbon as an efficient adsorbent for removal of methylene blue, RSC Adv. 7 (2017) 14395–14405.
[13] A.M. Obeidat, M.A. Gharaibeh, M. Obaidat, Solid-state supercapacitors with ionic liquid gel polymer electrolyte and polypyrrole electrodes for electrical energy storage, J. Energy Storage 13 (2017) 123–128.
[14] E.R. Dyartanti, A. Purwanto, I.N. Widiasa, H. Susanto, Ionic Conductivity and Cycling Stability Improvement of PVDF/Nano-clay Using PVP as Polymer Electrolyte Membranes for LiFePO4 Batteries, 2018https://doi.org/10.3390/membranes8030036.
[15] V.A. Online, et al., RSC Advances Isatin Thiosemicarbazones Promote Honeycomb Structure Formation in Spin-coated Polymer Films: Concentration Effect and Release Studies, 2017 12945–12952, https://doi.org/10.1039/c6ra28163j.
[16] A. Lamberti, Materials science in semiconductor processing flexible supercapacitor electrodes based on MoS2-intercalated rGO membranes on Ti mesh, Mater. Sci. Semicond. Process. (2017) 0–1, https://doi.org/10.1016/j.mssp.2017.06.046.
[17] X. Fu, et al., Inorganic and Organic Hybrid Solid Electrolytes for Lithium-ion Batteries, 2016 4236–4258, https://doi.org/10.1039/c6ce00171h.