

Influence of ionic liquid additives on the conducting and interfacial properties of organic solvent-based electrolytes against an activated carbon electrode

Kyungmin Kim¹, Yongju Jung² and Seok Kim^{1,*}

¹Department of Chemical and Biochemical Engineering, Pusan National University, Busan 609-735, Korea

²Department of Applied Chemical Engineering, Korea University of Technology and Education, Cheonan, 330-708, Korea

Article Info

Received 1 June 2014

Accepted 27 June 2014

*Corresponding Author

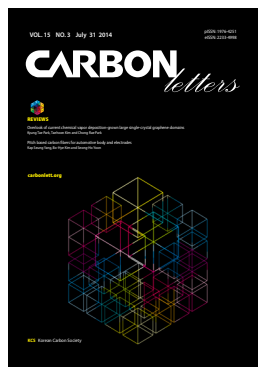
E-mail: seokkim@pusan.ac.kr

Tel: +82-51-510-3874

Open Access

DOI: <http://dx.doi.org/10.5714/CL.2014.15.3.187>

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.



<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

Copyright © Korean Carbon Society

Abstract

This study reports on the influence of N-butyl-N-methylpyrrolidinium tetrafluoroborate (PYR₁₄BF₄) ionic liquid additive on the conducting and interfacial properties of organic solvent based electrolytes against a carbon electrode. We used the mixture of ethylene carbonate/dimethoxyethane (1:1) as an organic solvent electrolyte and tetraethylammonium tetrafluoroborate (TEABF₄) as a common salt. Using the PYR₁₄BF₄ ionic liquid as additive produced higher ionic conductivity in the electrolyte and lower interface resistance between carbon and electrolyte, resulting in improved capacitance. The chemical and electrochemical stability of the electrolyte was measured by ionic conductivity meter and linear sweep voltammetry. The electrochemical analysis between electrolyte and carbon electrode was examined by cyclic voltammetry and electrochemical impedance spectroscopy.

Key words: organic solvent-based electrolytes, activated carbon, ionic liquid additives

1. Introduction

Electrochemical double layer capacitors (EDLCs) are energy storage systems which can be used in portable electronic devices, hybrid vehicles and for storing the energy generated by solar cells. The electrical charge is stored in the electrochemical double layer formed at the interface between electrode and electrolyte [1-6].

Commercial EDLCs have activated carbon as active materials and quaternary ammonium salts in acetonitrile or propylene carbonate as solvent. Generally, these EDLCs have operating voltages of 2.7-2.8 V [7,8]. Activated carbons are the most generally used electrode materials, due to their great adsorption ability and high surface area compared to other materials [9]. Another factor that influences the characteristics of an EDLC is the electrolyte component. Usually, the organic solvent used as the electrolyte must have a specific dielectric constant over 20, which influences ion association. Since ethylene carbonate (EC) solvent has a high dielectric constant ($\epsilon_r = 89.6$), it can effectively solve the salt. However, EC always has to be used with other solvents to drop its high melting point (Mp = 39°C). In contrast, linear carbonates such as 1,2-dimethoxyethane (DME), and dimethyl carbonate have low melting points and viscosity [10].

Many studies have been reported which aim to improve the electrochemical performance of EDLC by employing ionic liquids (ILs) [5,11-15]. ILs have an imidazolium, pyrrolidinium or sulfonium based cation and an anion such as tetrafluoroborate (BF₄⁻) or bis(trifluoromethylsulfonyl)imide (TFSI⁻). The properties of ILs include non-flammability, wide voltage window and high ionic conductivity. The most common IL is 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMImBF₄), which has a relatively low viscosity and high conductivity [16-18]. However, aromatic quater-

nary ammonium cations including imidazolium and pyridinium have relatively low cationic stability compared to pyrrolidinium [19].

Recently, it's been suggested that $\text{PYR}_{14}\text{BF}_4$ may display good electrochemical performance and could be an interesting additive candidate for EDLC. This study is to evaluate the effect of $\text{PYR}_{14}\text{BF}_4$ IL additive on the optimal proportion of EC/DME mixtures for application to EDLC.

2. Experimental

2.1. Carbon electrode and electrolyte

The carbon electrodes were prepared using activated carbons (MSP-20) as the active materials, carbon black as conducting agent and carboxymethyl cellulose/styrene-butadiene rubber as binder, in a glove box with Ar atmosphere. The materials were mixed in a fixed mass ratio and coated on nickel foam substrate. The composition was dried at 100°C in a vacuum oven for 12 h. The average active materials mass loading was about 10 mg/cm^2 .

EC and DME were purchased from DAEJUNG (>99%) and JUNSEI (>99%) respectively. Tetraethylammonium tetrafluoroborate (TEABF_4) salt was purchased from Aldrich Sigma and N-butyl-N-methylpyrrolidinium tetrafluoroborate ($\text{PYR}_{14}\text{BF}_4$) was supplied by C-tri Co. Ltd. The electrolytes were prepared by dissolving different weight ratios of $\text{PYR}_{14}\text{BF}_4$ into the EC/DME (1:1) co-solvent with 0.1 M TEABF_4 in a glove box. Then the prepared solutions were stirred for 24 h.

2.2. Measurement & analyse the characterization of EDLC

The ionic conductivity of the electrolytes mixture was evaluated by conductivity meter (ES-51, HORIBA Ltd.). Also, the bulk resistance and stability were evaluated by AC impedance spectroscopy over the frequency range from 100 kHz to 0.01 Hz and linear sweep voltammetry. In order to measure the operative voltages and capacitances of the EDLCs, cyclic voltammetry (CV) was carried out at 5 mVs^{-1} in three electrode systems. In this study, the working electrode was the prepared carbon electrode. Pt wire and Ag/AgCl (3 M NaCl) served as counter and reference electrodes, respectively.

3. Results and Discussion

3.1. Conducting property of electrolyte

Although EC exhibits high dielectric constant and viscosity, it always has to be used with another solvent due to its high melting point. So, for this purpose we selected 1,2-DME, a linear carbonate that has a low melting point ($M_p = -58^\circ\text{C}$). The optimal mixture ratio is 1:1 vol%. The incorporation of a co-solvent should result in the reduction of the melting point because of dipolar interaction [20].

Fig. 1 indicates that the ionic conductivities of the electrolyte at room temperature increased gradually with added amounts of $\text{PYR}_{14}\text{BF}_4$ additives, because it introduced numerous charge carriers into the electrolyte. The detailed values of conductivities are indicated in Table 1. When adding the $\text{TEABF}_4:\text{PYR}_{14}\text{BF}_4$ over 1:2, the ionic conductivity was not sharply changed due to the increase of ion carriers.

When preparing an electrolyte solution for a supercapacitor, electrochemical stability is an important factor. The stability of the electrolyte in this study was determined using CV at a scan rate of 10 mVs^{-1} . Pt wires were used as the working and counter electrode and the Ag/AgCl electrode was used as the reference electrode. As shown in Fig. 2,

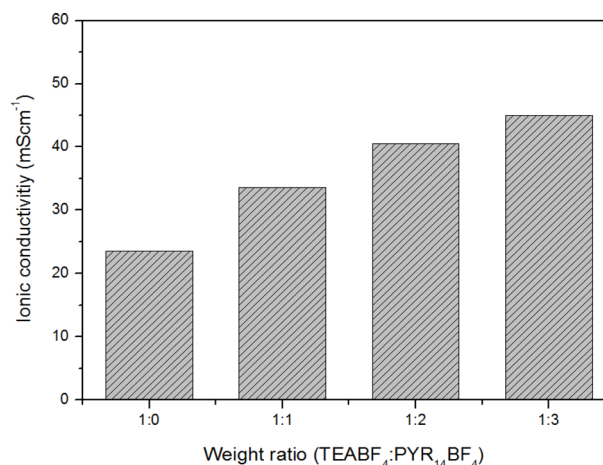


Fig. 1. Ionic conductivity evolution, versus the proportion of $\text{PYR}_{14}\text{BF}_4$ in wt% in EC/DME electrolytes with 0.1 M TEABF_4 . EC: ethylene carbonate, DME: dimethoxyethane.

Table 1. Ionic conductivity, resistance and capacitance for different proportions of $\text{PYR}_{14}\text{BF}_4$ in EC/DME (1:1) at room temperature

Proportion of $\text{PYR}_{14}\text{BF}_4$ ($\text{TEABF}_4:\text{PYR}_{14}\text{BF}_4$):	Ionic conductivity (mS cm^{-1})	Resistance (Ω)		Capacitance (F g^{-1})
		Bulk	Charge transfer	
1:0	23.60	24.77	65.22	38.98
1:1	33.60	11.55	61.44	69.35
1:2	40.50	2.20	41.74	92.55
1:3	45.00	20.91	101.69	77.21

EC: ethylene carbonate, DME: dimethoxyethane.

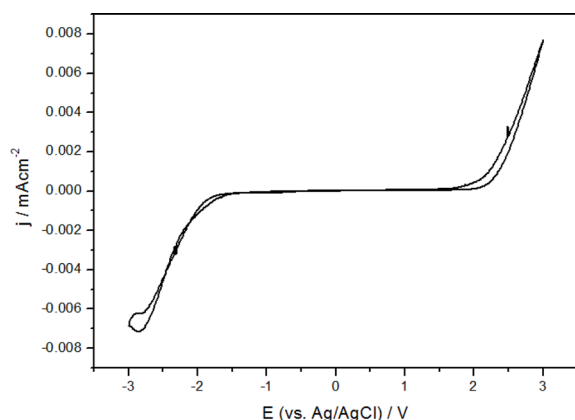


Fig. 2. Cyclic voltammogram at 5 mV s^{-1} of EC:DME (1:1) electrolyte with 0.1 M TEABF_4 and $\text{PYR}_{14}\text{BF}_4$ (weight ratio of TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ is 1:2). EC: ethylene carbonate, DME: dimethoxyethane.

the operative potential from -2 V to 2 V was electrochemically stable. The reason EC/DME with TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ (1:2) was selected was because it has good electrochemical performance, such as capacitance, rate capability and resistance. In the electrolyte stability measurement, EC/DME with TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ (1:2) was studied as an optimal electrolyte for a capacitor device.

3.2. Electrochemical performances of EDLCs

Fig. 3 shows the CV of EDLCs at a scan rate of 5 mV s^{-1} . The CV curves exhibit rectangular shapes that are typical of the capacitive properties of an EDLC. The specific capacitance of electrodes can be calculated according to the following equation.

$$C = \frac{\int IdV}{vm\Delta V}$$

C (Fg^{-1}) is the specific capacitance, I is the response current density (Acm^{-2}), v is the scan rate of potential (Vs^{-1}), m is the mass of the active materials in the working electrode (g), and ΔV is the operative voltage (V) in a three electrode system. The calculated capacitance values are indicated in Table 1.

As more $\text{PYR}_{14}\text{BF}_4$ ILs were added, the capacitances continuously increased, to 92.55 F/g . However, at the weight ratio of TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ over 1:2, the capacitance decreased, and may have been saturated. From these results, its clear $\text{PYR}_{14}\text{BF}_4$ ILs have positive effects on the electrolyte itself and electrode.

Fig. 4 displays the rate capability at different scan rates ($5, 10, 30, 50$ and 100 mV s^{-1}) between -0.5 V and 1.5 V . It can be observed that specific capacitances decreased with increasing scan rates. The ions of the electrolytes had difficulty diffusing into the inner pores of the carbon electrode at high scan rates, so only the external surface area of the electrodes could participate in the ion transfer reaction. At a high scan rate of over 30 mV s^{-1} the capacitance using the TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ over 1:2 declined sharply. This suggested that a number of ions obstructed the diffusion of ion charges. At the weight ratio of TEABF_4 : $\text{PYR}_{14}\text{BF}_4$ (1:2), good rate capability was confirmed, and the maximum

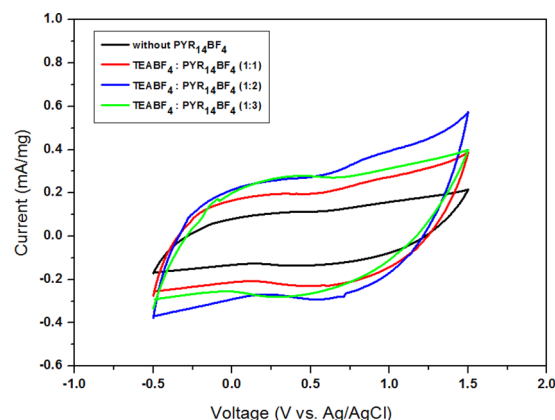


Fig. 3. Cyclic voltammogram curves of carbon electrode with different weight ratios of $\text{PYR}_{14}\text{BF}_4$ at a scan rate of 5 mV s^{-1} .

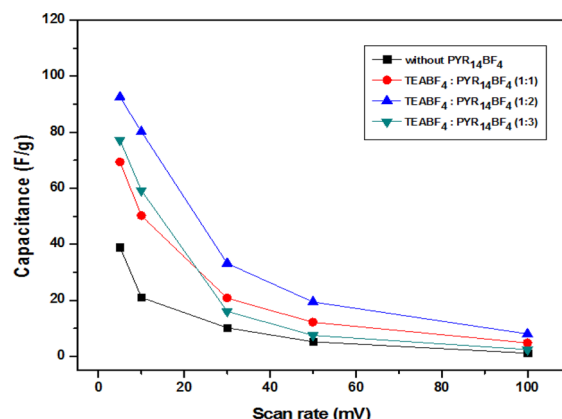


Fig. 4. Cyclic voltammogram curves of carbon electrode with different weight ratios of $\text{PYR}_{14}\text{BF}_4$ at different scan rate ($5, 10, 30, 50$ and 100 mV s^{-1})

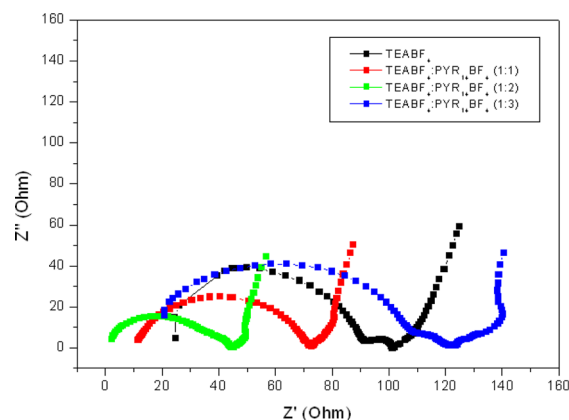


Fig. 5. Impedance plots of organic electrolytes containing different contents of $\text{PYR}_{14}\text{BF}_4$.

specific capacitance was 92.55 F/g at 10 mV s^{-1} and 8.01 F/g at 100 mV s^{-1} .

In Fig. 5, the impedance plots of co-solvents as a function of $\text{PYR}_{14}\text{BF}_4$ contents are displayed. The beginning plots at high frequency mean bulk resistances, and the size

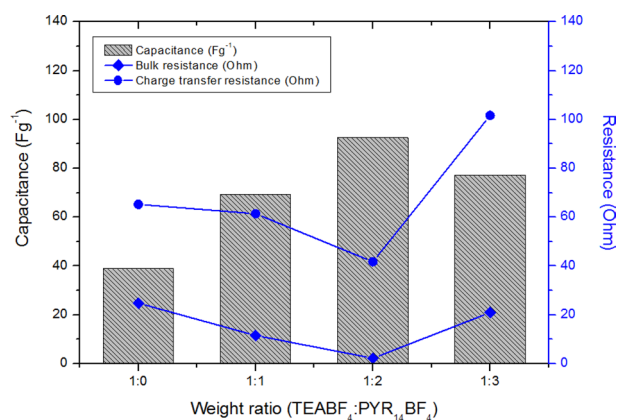


Fig. 6. Capacitance, resistances of electrochemical double layer capacitors using organic electrolytes containing different contents of Pyr₁₄BF₄.

of the semi-circle indicates charge transfer resistance. The calculated resistance values are shown in Table 1. When the Pyr₁₄BF₄ additives were added to the electrolyte, the bulk resistance declined and smaller sized semi-circle was observed. However, the bulk resistance and the charge-transfer resistance increased at a weight ratio of TEABF₄:Pyr₁₄BF₄ over 1:2. The charge transfer resistance is associated with gradients of potential between the ions in the electrolytes and the surface of the electrode. This phenomenon was caused by the kinetics of the electrochemical reactions and the diffusion of ions at the surface of the carbon electrode.

The capacitances have an effect on the charge transfer resistance [21,22]. Fig. 6 shows the variation of capacitance and resistances of bulk and charge-transfer produced by adding the Pyr₁₄BF₄ additives. As can be seen, Pyr₁₄BF₄ ILs can enhance the mobility of ion charge transfer and the capacitance of the carbon electrode. These results suggest that using the TEABF₄:Pyr₁₄BF₄ (1:2) in an organic electrolyte can produce an effective EDL and contribute to reducing the resistance at the carbon electrode, resulting in enhanced electrochemical performance.

4. Conclusions

In this paper, the effect of introducing Pyr₁₄BF₄ additive into an electrolyte against a carbon electrode was investigated for use in a capacitor. The addition of Pyr₁₄BF₄ into the organic solvent highly improved the ionic conductivity and reduced the interface resistance between the electrolyte and activated carbon electrode. Then, the Pyr₁₄BF₄ helped make a more compact EDL and so enhanced charge transfer throughout the activated carbon electrode. The maximum specific capacitance of the activated carbon electrode using the TEABF₄:Pyr₁₄BF₄ (1:2) additive in EC/DME (1:1) mixture electrolyte was 92.55 F g⁻¹. The electrochemical performance of the EDLC containing the TEABF₄:Pyr₁₄BF₄ (1:2) in EC/DME (1:1) electrolyte can be further optimized by considering a similar concept of using specialized supporting salts having large volume sized cation and anion.

Acknowledgments

This research was partly supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning, Korea (Grant No.: NRF-2011-0009007). This research was also supported by the BK21 PLUS Centre for Advanced Chemical Technology (Korea) (21A20131800002).

References

- [1] Oh MS, Park SJ, Jung Y, Kim S. Electrochemical properties of polyaniline composite electrodes prepared by in-situ polymerization in titanium dioxide dispersed aqueous solution. *Synth Met*, **162**, 695 (2012). <http://dx.doi.org/10.1016/j.synthmet.2012.02.021>.
- [2] Park SK, Kim S. Effect of carbon blacks filler addition on electrochemical behaviors of Co₃O₄/graphene nanosheets as a supercapacitor electrodes. *Electrochim Acta*, **89**, 516 (2013). <http://dx.doi.org/10.1016/j.electacta.2012.11.075>.
- [3] Kim KS, Park SJ. Electrochemical performance of graphene/carbon electrode contained well-balanced micro- and mesopores by activation-free method. *Electrochim Acta*, **65**, 50 (2012). <http://dx.doi.org/10.1016/j.electacta.2012.01.009>.
- [4] Gao ZH, Zhang H, Cao GP, Han MF, Yang YS. Spherical porous VN and NiO_x as electrode materials for asymmetric supercapacitor. *Electrochim Acta*, **87**, 375 (2013). <http://dx.doi.org/10.1016/j.electacta.2012.09.075>.
- [5] Park SK, Park SJ, Kim S. Preparation and capacitance behaviors of cobalt oxide/graphene composites. *Carbon Lett*, **13**, 130 (2012). <http://dx.doi.org/10.5714/CL2012.13.2.130>.
- [6] Kim JE, Park SJ, Kim S. Capacitance behaviors of polyaniline/graphene nanosheet composites prepared by aniline chemical polymerization. *Carbon Lett*, **14**, 51 (2013). <http://dx.doi.org/10.5714/CL2013.14.1.051>.
- [7] Ruch PW, Hahn M, Rosciano F, Holzapfel M, Kaiser H, Scheifelle W, Schmitt B, Novák P, Kötzer R, Wokaun A. In situ X-ray diffraction of the intercalation of (C₂H₅)₄N⁺ and BF₄⁻ into graphite from acetonitrile and propylene carbonate based supercapacitor electrolytes. *Electrochim Acta*, **53**, 1074 (2007). <http://dx.doi.org/10.1016/j.electacta.2007.01.069>.
- [8] Burke A. R&D considerations for the performance and application of electrochemical capacitors. *Electrochim Acta*, **53**, 1083 (2007). <http://dx.doi.org/10.1016/j.electacta.2007.01.011>.
- [9] Anouti M, Couadou E, Timperman L, Galiano H. Protic ionic liquid as electrolyte for high-densities electrochemical double layer capacitors with activated carbon electrode material. *Electrochim Acta*, **64**, 110 (2012). <http://dx.doi.org/10.1016/j.electacta.2011.12.120>.
- [10] Kim JH, Nam KW, Ma SB, Kim KB. Fabrication and electrochemical properties of carbon nanotube film electrodes. *Carbon*, **44**, 1963 (2006). <http://dx.doi.org/10.1016/j.carbon.2006.02.002>.
- [11] Berger C, Song Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J, Marchenkov AN, Conrad EH, First PN, de Heer WA. Electronic confinement and coherence in patterned epitaxial graphene. *Science*, **312**, 1191 (2006). <http://dx.doi.org/10.1126/science.1125925>.
- [12] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes

- A, Jia Y, Wu Y, Nguyen ST, Ruoff RS. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, **45**, 1558 (2007). <http://dx.doi.org/10.1016/j.carbon.2007.02.034>.
- [13] Palm R, Kurig H, Tönurist K, Jänes A, Lust E. Is the mixture of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate applicable as electrolyte in electrical double layer capacitors? *Electrochem Commun*, **22**, 203 (2012). <http://dx.doi.org/10.1016/j.elecom.2012.06.029>.
- [14] Francke R, Cericola D, Kötzt R, Weingarh D, Waldvogel SR. Novel electrolytes for electrochemical double layer capacitors based on 1,1,1,3,3,3-hexafluoropropan-2-ol. *Electrochim Acta*, **62**, 372 (2012). <http://dx.doi.org/10.1016/j.electacta.2011.12.050>.
- [15] Brandt A, Isken P, Lex-Balducci A, Balducci A. Adiponitrile-based electrochemical double layer capacitor. *J Power Sources*, **204**, 213 (2012). <http://dx.doi.org/10.1016/j.jpowsour.2011.12.025>.
- [16] Isken P, Dippel C, Schmitz R, Schmitz RW, Kunze M, Passerini S, Winter M, Lex-Balducci A. High flash point electrolyte for use in lithium-ion batteries. *Electrochim Acta*, **56**, 7530 (2011). <http://dx.doi.org/10.1016/j.electacta.2011.06.095>.
- [17] Perricone E, Chamas M, Cointeaux L, Leprêtre JC, Judeinstein P, Azais P, Béguin F, Alloin F. Investigation of methoxypropionitrile as co-solvent for ethylene carbonate based electrolyte in supercapacitors. A safe and wide temperature range electrolyte. *Electrochim Acta*, **93**, 1 (2013). <http://dx.doi.org/10.1016/j.electacta.2013.01.084>.
- [18] Abu-Lebdeh Y, Davidson I. High-voltage electrolytes based on adiponitrile for Li-ion batteries. *J Electrochem Soc*, **156**, A60 (2009). <http://dx.doi.org/10.1149/1.3023084>.
- [19] Oh MS, Kim S. Effect of dodecyl benzene sulfonic acid on the preparation of polyaniline/activated carbon composites by in situ emulsion polymerization. *Electrochim Acta*, **59**, 196 (2012). <http://dx.doi.org/10.1016/j.electacta.2011.10.058>.
- [20] Brandt A, Balducci A. The influence of pore structure and surface groups on the performance of high voltage electrochemical double layer capacitors containing adiponitrile-based electrolyte. *J Electrochem Soc*, **159**, A2053 (2012). <http://dx.doi.org/10.1149/2.074212jes>.
- [21] Kang J, Wen J, Jayaram SH, Yu A, Wang X. Development of an equivalent circuit model for electrochemical double layer capacitors (EDLCs) with distinct electrolytes. *Electrochim Acta*, **115**, 587 (2014). <http://dx.doi.org/10.1016/j.electacta.2013.11.002>.
- [22] Oh MS, Kim S. Synthesis and analysis of polyaniline/TiO₂ composites prepared with various molar ratios between aniline monomer and para-toluenesulfonic acid, *Electrochimica Acta*, **78**, 279 (2012). <http://dx.doi.org/10.1016/j.electacta.2012.05.109>.