Short communication

Are ionic liquids based on pyrrolidinium imide able to wet separators and electrodes used for Li-ion batteries?

Claudia Simona Stefan, Daniel Lemordant, Bénédicte Claude-Montigny, David Violleau*

Laboratoire de Physico-Chimie des Matériaux et des Biomolécules (LPCMB, EA 4244), Equipe Chimie-Physique des Interfaces et des Milieux Electrolytiques (CIME), Université F. Rabelais, Faculté des Sciences et Techniques, Parc de Grandmont, 37200 Tours, France

ABSTRACT

Surface free energy and contact angle measurements were conducted with a series of room temperature ionic liquids (RTILs) based on N,N′-alkyl-pyrrolidinium imide. Wetting characteristics of various separators (Celgard® and Separion®) and electrodes (LiCoO$_2$, Li$_4$Ti$_5$O$_{12}$ and graphite), commonly used in Li-ion batteries, were performed. Initially, the free surface energies were determined for both smooth polymeric materials, constituent of the separators, and pyrrolidinium RTILs. Experimental results and calculations show that (i) N-methyl-N-pentyl pyrrolidinium imide is the most wetting RTIL whatever the separator used, and that (ii) the separator wettability is one of the most important factor to take into account in electrochemical devices.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Many factors affect the performances of Li-ion batteries. One of the key factors for improving the cycling ability and the power of Li-ion batteries is the wettability of both electrodes and separators, especially when the temperature decreases. It has been previously shown that room temperature ionic liquids (RTILs) have a real potential for use in Li-ion batteries [1–5], but their use as single electrolyte, when mixed to a lithium salt, is held up because of their high viscosity at room temperature. At the opposite to organic solvents which are usually very volatile and highly flammable, RTILs exhibit low vapour pressure and are mostly non-flammable. Moreover, these compounds respect the environment, thanks to several physico-chemical properties conjugated with their chemical structure. Constituted only by organic cations and inorganic (seldom organic) anions, these room temperature molten salts present many advantages apart their non-flammability and negligible vapour pressure such as high chemical and thermal stability, a strong resistance toward both oxidation and reduction and correlatively a large electrochemical window.

Since a decade, researchers have focused their interest on RTIL thermo-physical properties for electrochemical applications in batteries (melting point, crystallisation temperature, thermal decomposition temperature, etc.) [1–8], but at our knowledge, no data are available concerning RTIL wetting properties. The only published results concerning wettability are dealing with conventional Li battery electrolytes based on organic compounds [9–10].

Characterization and prediction of wetting phenomenon by contact angle (CA) measurements and surface free energy (SFE) calculations are powerful analysis tools widely used for many applications [11], even if problems are encountered with the application of these methods and particularly the choice of an appropriate set of liquids and the ill-conditioning system of mathematical equations [12–14]. The thermodynamics of the sessile drop were first described by Young [15], which establishes the relation between the surface free energies of a liquid, a solid and a gas and the CA formed at the interface of the three phases. If the surface free energy of a liquid is easily obtained by surface free energy measurement, this is not the case of solids. For this reason, many methods were developed for the determination of the SFE of solids. The most often applied are those of Zisman [16], Owens–Wendt (OW) [17] and the most recent of van Oss–Chaudhury–Good (vOCG) [18–20].

The aim of this work is (i) to determine the surface free energy of N-alkyl-N-alkyl′-pyrrolidinium bis(trifluoromethane-sulfonyl)imide RTILs, and (ii) to determine the wettability of commercial separators and electrodes commonly used in the field of Li-ion batteries in the presence of these RTILs using the OW and vOCG methods.

* Corresponding author at: LPCMB (EA 4244) équipe CIME, Université François Rabelais, UFR des Sciences et Techniques, Parc de Grandmont, 37200 Tours, France. Tel.: +33 2 47 36 69 13; fax: +33 2 47 36 70 73.
E-mail address: david.violleau@univ-tours.fr (D. Violleau).

Table 1
Surface free energy (γ_L) in (mJ m^{-2}) of the reference liquids and their dispersive (γ_L^d), polar (γ_L^p), Lifshitz–van der Waals (γ_L^{LW}), electron acceptor (γ_L^+) and electron donor (γ_L^-) components.

	γ_L	γ_L^d	γ_L^p	γ_L^{LW}	γ_L^+	γ_L^-
Water (W)	72.8	21.8	51	21.8	25.5	25.5
Diiodomethane (D)	50.8	50.8	0.0	50.8	0.0	0.0
Formamide (F)	58.0	39.0	19.0	39.0	2.28	39.6

2. Experimental

2.1. Contact angle and surface free energy measurements

The contact angles were determined using the following reference liquids:

- Ultra pure water (W).
- Formamide (F) (HCONH$_2$, 99% GC, Sigma).
- Diiodomethane (D) (CH$_2$I$_2$, 99% GC, Sigma Aldrich).
- Four N-alkyl-N-alkyl'-pyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquids. For clarity, these RTILs are quoted in the following by the number of methyl groups in each alkyl side chain of the cation: Pxy = P13, P14, P15, P24. These ionic liquids were provided by Solvionic and dried under vacuum during 72 h before use.

The letters W, F and D were used to stand for relevant reference liquids and the corresponding contact angles are quoted as θ_W, θ_F and θ_D, respectively for water, formamide and diiodomethane at the air, liquid, solid interface. The values of SFE of the reference liquids and its components, used for the calculations, are displayed in Table 1.

Smooth polymeric materials (Goodfellow, Cambridge) were used for the characterization of the wetting properties of the ionic liquids: polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET). These polymers were chosen because they enter in the composition of the separators as shown in Table 2.

Three electrodes were analysed: a lithiated cobalt oxide cathode (LiCoO$_2$) and two anodes: a graphite and a lithium titanate oxide (Li$_4$Ti$_5$O$_{12}$). All electrodes are gift from the SAFT company.

The contact angles (CA) were measured according to the sessile drop method using a G-11 goniometer (Krüss, Germany), at room temperature (25 ± 2 °C). Between 8 and 10 measurements were performed for each sample. The lowest and the highest values were disregarded and the remaining values were used to calculate the arithmetic mean and the standard deviation.

For each sample, the standard deviation for CA was less than 3°, which involves a standard deviation for SFE calculation that never exceeds 6%.

The tensiometer K10ST (Krüss, Germany) was employed to measure the ionic liquid surface free energy, with the ring method. The method was calibrated to ensure accuracy and reliability, with

Table 2
Characteristics of the separators used in this study.

Separator	Thickness (μm)	Composition
Celgard® 2730	21	Monolayer PE membrane
Celgard® 2500	25	Monolayer PP membrane
Celgard® 2400	25	Monolayer PP membrane
Celgard® 2320	20	Trilayer membrane with one PE layer between two PP layers
Separion®	30	Ceramically (Al$_2$O$_3$, SiO$_2$) impregnated and coated polyethylene terephthalate (PET) polymer non-woven film

pure water. Experimental surface free energy of 72.5 mJ m^{-2} was obtained, in good agreement with values reported in Table 1.

2.2. SFE calculation

Owens–Wendt (OW) and van Oss–Chaudhury–Good (vOCG) methods were used for the calculation of the surface free energy (SFE) of the separators (using reference liquids) and of ionic liquids (using smooth polymeric materials). For the three electrodes under study, calculation of SFE was not performed because the penetration of the liquid into the electrode material was too rapid. Contact angles mentioned are "initial" contact angles, i.e. measured just after the drop was deposited onto the surface.

2.2.1. Owens–Wendt (OW) method [17]

For this method, a set of two liquids (one dispersive and one polar liquid) is employed, which leads to a couple of linear equations. Calculation of SFE is based on the following equations:

$$0.5(1 + \cos\theta)\gamma_{L,i} = (\gamma_S^d \gamma_{L,i}^d)^{0.5} + (\gamma_S^p \gamma_{L,i}^p)^{0.5} \quad \text{for } i = 1, 2 \tag{1}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{2}$$

The superscripts d and p are related respectively to the dispersive and polar components of the SFE. The subscripts L and S refer to the liquid and solid, respectively.

2.2.2. van Oss–Chaudhury–Good (vOCG) method [18]

This method uses three surface free energies, instead of two: the Lifshitz–van der Waals component (γ_S^{LW}), the electron acceptor or Lewis acid component (γ_S^+) and the electron-donor or Lewis base component (γ_S^-).

As a consequence, a set of three liquids ($i = 1, 2, 3$) is required to calculate the SFE components for the solid, by mean of the following equations:

$$0.5(1 + \cos\theta)\gamma_{L,i} = (\gamma_S^{LW} \gamma_{L,i}^{LW})^{0.5} + (\gamma_S^+ \gamma_{L,i}^-)^{0.5} + (\gamma_S^- \gamma_{L,i}^+)^{0.5} \tag{3}$$

$$\gamma_S = \gamma_S^{LW} + 2(\gamma_S^- \gamma_S^+)^{0.5} \tag{4}$$

Calculation of the interfacial free energy between the solid and liquid (γ_{SL}) was performed using the Young's equation:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}. \tag{5}$$

3. Results and discussion

3.1. Characterization of smooth polymeric reference materials

Contact angle values obtained with the reference liquids W, D and F for the smooth polymeric materials are displayed in Table 3. The corresponding SFE values obtained with OW and vOCG methods for different sets of measuring liquids are listed in Tables 4 and 5.

Due to the higher surface energy of W compared to D and F, water contact angles on all polymer surfaces are higher than those obtained using D and F. It can be seen that PP presents a higher contact angle than PET in the presence of W and F but a lower contact angle in the presence of D. This can be attributed to the fact that W and F have both polar and dispersive components, while D has mostly dispersive component. Since W, D and F have higher surface

Table 3
Contact angles on smooth polymer surfaces.

	θ_W (°)	θ_D (°)	θ_F (°)
PE	93.6 ± 1.0	54.5 ± 2.9	76.8 ± 1.5
PP	91.8 ± 1.8	49.5 ± 2.1	78.7 ± 2.8
PET	57.5 ± 1.8	50.8 ± 2.3	53.2 ± 2.1

Table 4

Surface free energy (γ_S) and its dispersive (γ_S^d) and polar (γ_S^p) components in mJ m^{-2} for smooth polymeric materials with the OW method (Eqs. (1) and (2) in the text).

	γ_S	γ_S^d	γ_S^p
W/D			
PE	32.9	31.7	1.2
PP	35.7	34.5	1.2
PET	50.0	33.8	16.2
W/F			
PE	22.7	19.0	3.7
PP	20.8	15.0	5.8
PET	43.1	13.0	30.1
D/F			
PE	31.7	31.7	0.01
PP	34.7	34.5	0.2
PET	39.1	33.8	5.3

energies than all studied solid surfaces, all liquids wet only partially these polymers.

The SFE calculated using the OW method (Table 4) and the combination of three liquids (WD, WF and DF) require some comments:

- the SFE values for PE and PP, calculated with W/D and D/F combinations of reference liquids are very close together and in agreement with published values [20] (Table 6). This result confirms that theses two polymers, as expected, are almost apolar.
- the SFE values for PET are highly dependent on the set of chosen liquids. This can be attributed to the heterogeneity of the surface and/or to the roughness of the surface at the microscopic level. Nevertheless, γ_S value for the D/F combination is in the range of literature data (Table 6). Establishment of hydrogen bonds between PET and W may explain the high polar component calculated when W/D or W/F are used as couple of reference liquids.
- the values for PP and PE with the W/F set are very far from most literature data: this confirms the fact, as previously noted [12,21], that the W/F combination is not an adequate choice because both water and formamide are polar liquids.

The results obtained with the vOCG method are in relative good agreement with published data for these polymeric materials, and are close from those obtained with the OW method, especially for γ_S and γ_S^d values. It could be pointed out that small differences between vOCG and OW calculations have been previously observed by Zenkiewicz [14] using other materials. As noticed by Della Volpe and Siboni [13], a systematic overvaluation is observed for the SFE basic component γ_S^-.

The results reported in Tables 4 and 5 show, as already mentioned in the literature [12–14,21], the relative dependence of SFE results on the liquid set used for calculations.

Table 5

Surface free energy (γ_S) and its Lifshitz–van der Waals (γ_S^{LW}), Lewis acid (γ_S^+) and Lewis base (γ_S^-) components in mJ m^{-2} for smooth polymeric materials with the vOCG method (Eqs. (3) and (4) in the text).

W/D/F	γ_S	γ_S^{LW}	γ_S^+	γ_S^-
PE	33.3	31.7	0.2	3.8
PP	39.0	34.5	0.8	6.0
PET	37.7	33.8	0.1	29.2

Table 6

Range of SFE values for the three studied polymeric materials, from Ref. [13,19].

	γ_S (mJ m^{-2})
PE	27.0–36.3
PP	28.0–34.1
PET	37.4–46.5

Table 7

Surface free energy of the Pxy RTILs (in mJ m^{-2}), contact angles ($\circ$) at the liquid/polymer/air interface, dispersive (γ_L^d) and polar (γ_L^p) components of the SFE calculated with the OW method (Eqs. (1) and (2) in the text) and interfacial free energy (γ_{SL}) determined by Young's equation (mJ m^{-2}) (Eq. (5) in the text).

	P13	P14	P15	P24
γ_L	36.5	34.5	34.6	35.2
PE				
θ	52.2 ± 0.6	50.8 ± 1.3	49.5 ± 2.3	51.1 ± 2.1
γ_L^d	19.6	17.6	18.3	18.4
γ_L^p	16.9	16.9	16.2	16.7
γ_{SL}	10.5	11.1	10.4	10.8
PP				
θ ($\circ$)	56.7 ± 1.2	58.8 ± 2.2	51.4 ± 2.4	53.4 ± 1.0
γ_L^d	15.7	12.9	15.8	15.7
γ_L^p	20.8	21.6	18.8	19.5
γ_{SL}	15.7	17.8	14.1	14.7
PET				
θ	57.7 ± 2.0	59.8 ± 1.3	54.9 ± 1.2	57.2 ± 0.6
γ_L^d	7.1	5.4	6.7	6.5
γ_L^p	29.4	29.1	27.9	28.7
γ_{SL}	19.6	21.7	19.2	20.0

In the present article, the following set of SFE values, expressed in mJ m^{-2}, for reference polymeric materials are retained:

PE : $\gamma_S = 32.9$, $\gamma_S^d = 31.7$, $\gamma_S^p = 1.2$
PP : $\gamma_S = 35.7$, $\gamma_S^d = 34.5$, $\gamma_S^p = 1.2$
PET : $\gamma_S = 39.1$, $\gamma_S^d = 33.8$, $\gamma_S^p = 5.3$

3.2. Characterization of RTILs: P13, P14, P15 and P24

Table 7 presents SFE values of the four RTILs obtained from surface free energy measurements and from CA of sessile drops deposited onto reference polymeric materials. When only γ_L values are considered, no significant differences are observed between the four RTILs, this is confirmed by the narrow range of CA values ($\langle 49.5–59.8^\circ \rangle$) obtained for all polymeric surfaces. Nevertheless P15 exhibits the lowest CA values for the three polymers, indicating that P15 wets all polymers better than the other RTILs. This observation is confirmed by the lowest value of the interfacial free energy γ_{SL} for P15 which is an indicator of the "compatibility" of a liquid for a solid in contact. This means that when γ_{SL} is low a good adhesion is expected. On the contrary P14 presents the highest γ_{SL} values. Dispersive and polar components are dependent on the nature of the polymer used, but in all case, RTILs present a high polar SFE component which is due to their ionic structure. P15 exhibits the lowest polar SFE component whatever the polymer employed. As indicated by the higher values of the contact angle, PET is less wet than PP and PE which is in accordance with the following consideration: the higher the difference between the surfaces energies of the liquid and the solid is, the lower the wetting is expected.

CA measurements have been performed using an electrolyte commonly employed in Li ion-batteries: LiPF$_6$ 1 M in the alkyl carbonate mixture EC/PC/3DMC. The CA are 38.3 ± 1.2 for PE and 49.3 ± 1.9 for PP. Even if further investigations are needed, it can be noticed that incorporation of RTILs in a conventional electrolyte in order to improve its security will not decrease the wettability dramatically.

3.3. Characterization of separators

CA measurements obtained by the sessile drop method on the separators under study are reported in Table 8. For the four Celgard® separators, the CA increases in the order:

$$\theta_D < \theta_F < \theta_W,$$

Table 8
CA measurements (in degree) of sessile drops of W, D and F on electrochemical separators.

	Celgard® 2320	Celgard® 2400	Celgard® 2500	Celgard® 2730	Separion®
θ_W	110.3 ± 1.3	104.4 ± 2.0	109.4 ± 1.6	99.5 ± 1.9	60.4 ± 2.2
θ_D	57.4 ± 2.2	56.5 ± 2.2	61.5 ± 2.0	54.6 ± 1.4	34.9 ± 1.5
θ_F	91.1 ± 1.4	88.8 ± 1.8	85.2 ± 1.4	80.8 ± 2.1	30.2 ± 1.6

which is the same as the liquid polarity. In the presence of water, the CA exceeds 90° (θ_W is in the range of 99.5–110.3°) showing the hydrophobic character of the Celgard® separators. Even if no great differences are observed between the Celgard separators, Celgard® 2730 presents the lowest CA for all liquids higher wettability is due to its chemical composition based on PE which has a higher surface free energy than PP.

Because of the high wettability and the porosity of the Separion® separator, the liquids penetrate slowly into the membrane: usually the liquid drops disappeared in 5–10 min. Consequently, CA have to be measured just after droplet deposition. As compared to Celgard®, Separion® separator clearly exhibits smaller CA independent of the reference liquid used. Its high wettability is certainly more related to the Al$_2$O$_3$ and SiO$_2$ coating than to the use of PET instead of PE or PP. Metal and silica oxides have very high SFE as compared to polymeric material and thus are more easily wet.

SFE values (in mJ m^{-2}) of the separators calculated with the OW and vOCG methods and with the different sets of reference liquids are presented in Table 9. As mentioned above, SFE values obtained with the W/F are not suitable because of polarity of the two liquids. For Celgard® separators, when W/D and D/F sets are used, SFE values (calculated with the OW method) are close together and show that they are non-polar ($\gamma_S^p \approx 0$), in accordance with their composition (PP for Celgard® 2320, 2400, 2500 and PE for Celgard® 2730).

SFE values calculated with the vOCG method lead to similar results for the four separators. For Celgard® separators, whatever the method of calculation used, γ_S^d and γ_S follow the order:

Celgar®2500 < Celgard®2320 < Celgard®2400 < Celgard®2730

As a conclusion, better wetting is expected for the Celgard® 2730 in fair accordance with experimental CA measurements reported in Table 8.

Table 9
SFE and its dispersive and polar components values for the electrochemical separators under study, calculated with the OW and vOCG methods (mJ m^{-2}) and with different liquid sets.

	Celgard® 2320	Celgard® 2400	Celgard® 2500	Celgard® 2730	Separion®
W/D					
γ_S^d	30.07	30.59	27.71	31.67	42.07
γ_S^p	0.06	0.04	0.00	0.33	11.38
γ_S	30.13	30.63	27.71	32.00	53.45
W/F					
γ_S^d	18.05	15.64	25.46	21.29	41.24
γ_S^p	0.30	1.54	0.01	1.53	11.67
γ_S	18.35	17.18	25.47	22.82	52.91
D/F					
γ_S^d	30.07	30.59	27.71	31.67	42.07
γ_S^p	1.48	1.03	0.04	0.04	11.05
γ_S	31.55	31.62	27.75	31.71	53.12
W/D/F					
γ_S^{LW}	30.07	30.58	27.71	31.67	42.07
γ_S^+	1.21	1.27	0.08	0.20	1.76
γ_S^-	0.54	0.94	0.05	0.13	11.85
γ_S	31.69	31.81	27.84	32.00	51.22

Table 10
Surface porosity $(1 - \varphi_S)$ in % of the Celgard® separators evaluated by the Cassie–Baxter approach for a composite surface (Eq. (6) in the text).

Celgard® 2320	33%
Celgard® 2400	22%
Celgard® 2500	31%
Celgard® 2730	11%

γ_S values for the four Celgard® are lower than those obtained for the smooth polymeric materials with the same sets of reference liquids. This observation could be explained by surface porosity of separators. For porous material, the Cassie–Baxter approach [22] can be employed to calculate the separator surface porosity. It will be assumed that the porous separator is a composite material formed of smooth polymeric material and holes which are not filled by the liquids. This leads to the formation of a composite surface with trapped air pockets. The solid polymeric surface occupies a fraction of the total area equal to φ_S and presents an intrinsic contact angle equal to θ'. The freely suspended fraction in contact with air has the complementary area fraction $(1 - \varphi_S)$ and a contact angle of 180°. Applying the Cassie–Baxter equation to this system leads to:

$$\varphi_S = \frac{1 + \cos\theta}{1 + \cos\theta'} \tag{6}$$

where θ is the apparent contact angle of the liquid drop deposited on the Celgard® separator. The surface porosity of the different separators, expressed as $(1 - \varphi_S)$ in % and calculated by Eq. (6) is displayed in Table 10.

Compared to the other separators, Celgard® 2730 exhibits the lowest surface porosity (11%). This result is in good agreement with the best wetting properties of this separator previously mentioned, as it presents the lowest surface fraction in contact air. From the same point of view, Celgard® 2500 and 2320 present the highest surface porosity (31 and 33%, respectively) and hence the lower wettability.

Whatever the calculation method and the choice of the reference liquids, SFE values for Separion® separator are very close together (Table 8). This separator presents higher dispersive and polar SFE components than Celgard® separators in tight relation with its great wettability. Because of liquid penetration into the Separion® separator, the Cassie–Baxter approach cannot be used and the surface porosity cannot be evaluated.

3.4. Wettability of separators by RTILs

The contact angles of the four pyrrolidinium imides, determined by the sessile drop method at the air–separator interface, are reported in Table 11. Using the Young's equation, Eq. (5) in the text, and γ_L and γ_S previously determined, the interfacial free energy (γ_{SL}) at the RTIL/separator interfaces have been calculated and the results are displayed in Table 11.

For all RTILs, the Celgard® 2730 membrane presents the lowest CA values, indicating that it is better wet than the other Celgard® for which no clear tendency can be drawn. Among RTILs, P15 exhibits once again the lowest CA values for all Celgard® separators, while the highest CA values are obtained with P13.

Considering γ_{SL} data, the lowest values are obtained for the Celgard® 2730 membrane which denotes a good compatibility between the P13, P14 and P15 liquids and the solid material. For P24, the lowest γ_{SL} value is obtained with the Celgard® 2500. In terms of wettability, the best combination is obtained with P15 and Celgard® 2730 as the CA is only 38.4° and the interfacial energy as low as 4.9 mJ m^{-2}.

CA measurements using Separion® membranes were difficult to perform because the drop spreads quickly owing to the fact that the

Table 11

Wettability of separators by pyrrolidium imide RTILs: contact angles (°) and interfacial free energy, γ_{SL} in mJ m^{-2}, determined by the Young's equation (Eq. (5) in the text).

	Celgard® 2320	Celgard® 2400	Celgard® 2500	Celgard® 2730	Separion®
P13					
θ	60.9 ± 1.1	60.9 ± 1.0	67.3 ± 0.8	53.1 ± 0.7	21.6 ± 2.8
γ_{SL}	12.4	12.9	13.6	10.1	n.c.
P14					
θ	60.5 ± 0.7	59.0 ± 1.3	58.5 ± 2.3	46.9 ± 1.7	15.8 ± 2.1
γ_{SL}	13.1	12.9	9.7	8.4	n.c.
P15					
θ	49.0 ± 0.4	50.5 ± 1.4	52.6 ± 0.6	38.4 ± 1.4	t.w.
γ_{SL}	7.4	8.6	6.7	4.9	n.c.
P24					
θ	52.3 ± 0.7	56.9 ± 1.0	53.9 ± 0.6	46.4 ± 1.1	t.w.
γ_{SL}	8.6	11.4	7.0	7.7	n.c.

t.w., total wetting; n.c., not calculated.

Table 12

CA measurements (°) of electrodes with pyrrolidinium imide RTILs.

	P13	P14	P15	P24
LiCoO$_2$	18.3 ± 0.7	17.1 ± 0.2	15.1 ± 0.6	14.7 ± 0.4
Graphite	21.1 ± 0.7	20.6 ± 1.6	17.9 ± 0.8	20.2 ± 0.7
Li$_4$Ti$_5$O$_{12}$		Total wetting		

liquids penetrate into the membrane pores. With P15 and P24, the sessile drops disappeared in few seconds preventing any CA measurement. The penetration of P13 and P14 liquids into the pores was slower and so the initial CA (i.e. at time zero) could be measured: CA were 21.6° and 15.8° respectively for P13 and P14. These results show the great wettability of Separion® membrane even by high surface free energy liquids. Nevertheless, further investigations are needed for improving the characterization of this porous separator. Sorption measurements using the Washburn method [23] would be probably a more appropriate method to study this kind of membrane.

3.5. Wettability of electrodes

As the composite electrodes are also easily wet by the RTILs, only the initial CA values could be determined. The CA obtained for the LiCoO$_2$ and graphite electrodes are reported in Table 12. In the case of the Li$_4$Ti$_5$O$_{12}$ electrode, no values have been recorded as the wetting was complete. CA values ranging from 14.7° to 21.1° are low and close together. This reveals that the composites electrodes are well wet by all alkyl pyrrolidinium ionic liquids and that the addition of any wetting agent is not required. Moreover, the impact of the wettability on the Li-ion batteries performance is more relevant for separators than for electrodes.

4. Conclusion

Generally speaking, SFE values depend on both the calculation methods and the choice of the reference liquid sets used in the CA measurements. RTILs present SFE values are in the range 34.5–36.5 mJ m^{-2}, with high polar components owing to their ionic structure. CA and interfacial free energy (γ_{SL}) values show that P15 is among the four pyrrolidinium imides under study, the ionic liquid which is able to wet the most easily smooth polymeric materials such as PE or PP.

Celgard® separators, which are hydrophobic and non-polar porous membranes, present SFE values ranging from 27 to 32 mJ m^{-2}, characteristic of this kind of polyolefine materials. Celgard® 2730 presents the lowest CA and γ_{SL} values with all measuring liquids used, showing its high wettability in particularly using with P15 as RTIL. The Cassie–Baxter approach highlighted the role of the surface porosity for understanding the wetting behavior of Celgard® separators. The Separion® membrane was characterised by its superior wettability which makes the determination of the CA difficult and even impossible using the sessile drop method. The same is also valid for the studied composite electrodes for which no problem of wetting by the high free energy ionic liquids has been found. Nevertheless, further investigations using capillary rise or thin layer wicking techniques will be required to investigate in detail the comportment of these materials in the presence of ionic liquids.

CA and SFE measurements for pyrrolidinium imide RTILs on both separators and electrodes, show that if wettability problems occur in Li-ion batteries, especially at low temperatures, the origin will be more likely the porous separators than the composite electrodes.

References

[1] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim. Acta 51 (2006) 5567–5580.
[2] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, WILEY-VCH, 2002.
[3] A. Fernicola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, J. Power Sources 174 (2007) 342–348.
[4] O.O. Okoturo, T.J. VanderNoot, J. Electroanal. Chem. 568 (2004) 167–181.
[5] D.R. MacFarlane, K.R. Seddon, Ionic Aust. J. Chem. 60 (2007) 3–5.
[6] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164–4170.
[7] G.B. Appetecchi, S. Scaccia, C. Tizzani, F. Alessandrini, S. Passerini, J. Electrochem. Soc. 153 (9) (2006) A1685–A1691.
[8] D.R. MacFarlane, P. Meakin, N. Amini, M. Forsyth, J. Phys. Condens. Matter 13 (2001) 8257–8267.
[9] M.S. Wu, T.L. Liao, Y.Y. Wang, C.C. Wan, J. Appl. Electrochem. 34 (2004) 797–805.
[10] M. Sugita, M. Yoshio, Y. Ito, Abstract no. 145 in Proceedings of the 12th International Meeting on Lithium Battery, Nara, Japan, 2004.
[11] R.J. Good, J. Adhes. Sci. Technol. 6 (12) (1992) 1269–1302.
[12] C. Della Volpe, D. Maniglio, S. Siboni, M. Morra, J. Adhes. Sci. Technol. 17 (11) (2003) 1477–1505.
[13] C. Della Volpe, S. Siboni, J. Adhes. Sci. Technol. 14 (2) (2000) 235–272.
[14] M. Zenkiewicz, Polymer Testing 26 (2007) 14–19.
[15] T. Young, Philos. Trans. Roy. Soc. Lond. 95 (1805) 65–87.
[16] W.A. Zisman, ACS Adv. Chem. 43 (1961) 1–51.
[17] D.K. Owens, R.C. Wendt, Estimation, J. Appl. Polym. Sci. 13 (1969) 1741–1747.
[18] C.J. van Oss, R.J. Good, M.K. Chaudhury, Langmuir 4 (1988) 884–891.
[19] C.J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker Inc., New York, 1994.
[20] I. Yildirim, Surface free energy characterization of powders, PhD Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2001.
[21] M. Zenkiewicz, Int. J. Adhes. Adhes. 25 (2005) 61–66.
[22] A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40 (1944) 546–551.
[23] E.W. Washburn, Phys. Rev. 17 (1921) 273–293.