

PAPER

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Novel fluorine-free 2,2'-bis(4,5-dimethylimidazole) additive for lithium-ion poly(methyl methacrylate) solid polymer electrolytes

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In this report, we study the effect of the addition of fluorine-free 2,2'-bis(4,5-dimethylimidazole) (BDI) on lithium-ion solid polymer electrolytes based on lithium nitrate and poly(methyl methacrylate) (PMMA). Confocal Raman spectroscopy and theoretical Raman calculations were performed to study lithium dissociation and the interaction mechanism of the lithium and nitrate ions with the BDI additive. Additionally, X-ray diffraction analysis showed that the mean coherence length of the PMMA chains is influenced by the BDI concentration. The incorporation of the BDI additive favors the dissociation of lithium salt leading to a maximum enhancement on the lithium conductivity of up to $1.88 \times 10^{-4} \text{ S cm}^{-1}$ for a critical BDI addition of $\sim 5\%$ with respect to PMMA, which is very high in comparison with the conductivities of $\sim 10^{-4} \text{ S cm}^{-1}$ usually observed for these solid polymer electrolytes.

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Introduction

The use of solid polymer electrolytes (SPE) in lithium ion batteries as an alternative to liquid electrolytes is currently being studied due to the advantages of safer design, hermetic sealing, flame-resistance and shape suitability.^{1–3} Improvements in the performance of these solid polymer electrolytes are related to reducing the crystallinity and decreasing the glass transition temperature of the polymer. Poly(methyl methacrylate) (PMMA) is usually preferred as a solid polymer electrolyte host because of its great amorphicity, ability to coordinate to lithium through its carbonyl group, high transparency and light weight.^{4,5} The inclusion of additive materials such as nano-particle fillers has shown an enhancement in the lithium salt dissociation leading to higher conductivity in solid polymer electrolytes.^{6–15}

On the other hand, liquid electrolytes based on imidazole-derived lithium salts such as lithium 4,5-dicyano-2-(trifluoromethyl) imidazolate (LiTDI)^{16,17} or trilithium 2,2',2''-tris (trifluoromethyl)benzotris (imidazolate) (Li₃BTI)¹⁸ are still preferred due to their excellent lithium conductivity of up to $\sim 10^{-3} \text{ S cm}^{-1}$ in liquid organic solvents. The purpose of using lithium imidazole salts is to weaken the chemical bonds between the anion and lithium ion, in order to prevent ionic-pair formation, thus enhancing the lithium transference number and the conductivity. In addition, polymer electrolytes based on lithium conductive imidazole salts have

also been studied, exhibiting lithium conductivities as high as 10^{-4} to $10^{-3} \text{ S cm}^{-1}$.^{19,20}

However, in addition to non-liquid electrolytes, there is still the need to study imidazole compounds which do not comprise fluorine atoms, in order to meet the safety requirements of lithium batteries. Regarding this, general imidazole compounds have also shown a strong interaction through their amine (N–H) groups, mediated by hydrogen bonds, with most typical inorganic anions used in lithium electrolytes such as nitrate^{21,22} and perchlorate.²³ However, neither of them has been used for this purpose in lithium solid polymer electrolyte applications. Up to now, there are no reports studying the effect of adding fluorine-free imidazole molecular additives into solid polymer electrolytes using simple lithium inorganic salts on the lithium ion conductivity.

In this report, we study the influence of the addition of 2,2'-bis(4,5-dimethylimidazole) (BDI) as a molecular additive using lithium nitrate (LiNO₃) as the salt source and PMMA as the polymer host, in order to improve the lithium conductivity in these solid polymer electrolytes. A one-step preparation is reported for different BDI concentrations, followed by a complete structural and electrical characterization by means of confocal Raman spectroscopy, infrared spectroscopy, differential scanning calorimetry, X-ray diffraction and electrochemical impedance spectroscopy.

Materials and methods

Poly(methyl methacrylate) (PMMA) 15.000 *M_w*, 2,2'-bis(4,5-dimethylimidazole) (BDI) and lithium nitrate (LiNO₃) 99.9% provided by Sigma-Aldrich were dissolved separately in anhydrous tetrahydrofuran (THF) under vigorous stirring at room

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temperature. The solutions were mixed in order to obtain a final PMMA : LiNO₃ : BDI weight ratio of 100 : 7 : 0, 3, 5, 7, 10, 15 and were stirred for 6 hours at $T \sim 50^\circ\text{C}$ until dry and then vacuum dried at $T \sim 80^\circ\text{C}$ for 20 hours to remove residual solvent. The dried powder samples were finally pressed into pellets under a pressure of 50 kN cm^{-2} to obtain the polymer composites named BDI- X , where $X = 0, 3, 5, 7, 10$ and 15 , respectively.

FT-IR spectroscopy was performed using a Shimadzu Prestige 21 following prior dilution in KBr and pelletizing. FT-IR spectra were recorded in the range of $400\text{--}4000\text{ cm}^{-1}$ by averaging 20 scans with a resolution of 4 cm^{-1} . Confocal Raman spectroscopy was performed using a WITec Alpha 300-RA confocal Raman spectrometer. The laser wavelength used in this experiment was 785 nm to avoid sample fluorescence and the laser power was set to $\sim 10\text{ mW}$, in order to avoid sample decomposition. Raman spectra were obtained by averaging a set of 400 spectra with 0.2 s integration time for each spectra. Raman spectra simulation was performed using density functional theory (DFT)^{24,25} using the hybrid exchange correlation potential B3LYP^{26–29} for a 6–31++G(d,p) basis set, as implemented in Gaussian 09.³⁰ X-ray powder diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer with CuK α radiation in the $2\theta = 5\text{--}50^\circ$ range using 2θ steps of 0.02° with a 3 s integration time per step. Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC-60 with a 5°C min^{-1} ramp rate in the $T = 20\text{--}150^\circ\text{C}$ temperature range. Electrochemical impedance spectroscopy (EIS) measurements

were performed for the BDI- X pellets with a 1.2 cm diameter and 0.2 cm thickness using sputtered gold blocking electrodes. EIS data were obtained using a 10 mV voltage amplitude in the $0.1\text{ Hz--}1\text{ MHz}$ frequency regime at 20°C using a Gamry Reference 3000 impedance analyzer. Data processing was performed using Echem Analyst software.

Results and discussion

FT-IR spectra for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 are shown in Fig. 1a. In all cases, the peaks ascribed to PMMA showed no drastic variations from $\sim 750, 966\text{--}989, 1150\text{--}1273, 1400\text{--}1490$ and 1732 cm^{-1} , attributed to the $\delta(\text{CH}_2)$ deformation, $\nu(\text{C=O})$ stretching, $\nu(\text{O--CH}_3)$ stretching, $\delta(\text{CH}_2, \text{CH}_3)$ deformation and $\nu(\text{C=O})$ stretching modes, respectively.^{31,32} Moreover, the peaks ascribed to BDI showed no drastic variations from $\sim 947\text{--}977, 1209, 1384$ and 1603 cm^{-1} , attributed to the $\delta(\text{C--H})$ out of plane bending, $\nu(\text{C--N})$ stretching, $\delta(\text{C--H})$ bending and $\nu(\text{C=C})$ stretching modes, respectively.³³

Raman spectra for BDI- X samples with $X = 0, 3, 5, 7, 10$ and 15 are shown in Fig. 1b. In all cases, the peaks ascribed to PMMA showed no drastic variations from $\sim 605, 817, 990, 1475$ and 1720 cm^{-1} , attributed to the $\nu(\text{C--C})$ stretching, $\delta(\text{O--C=O})$ deformation, $\nu(\text{O--CH}_3)$ stretching, $\delta(\text{H--C--H})$ deformation and $\nu(\text{C=O})$ stretching modes, respectively. Moreover, the peaks ascribed to BDI showed no drastic variations from $\sim 1039, 1263, 1583$ and 1629 cm^{-1} , attributed to

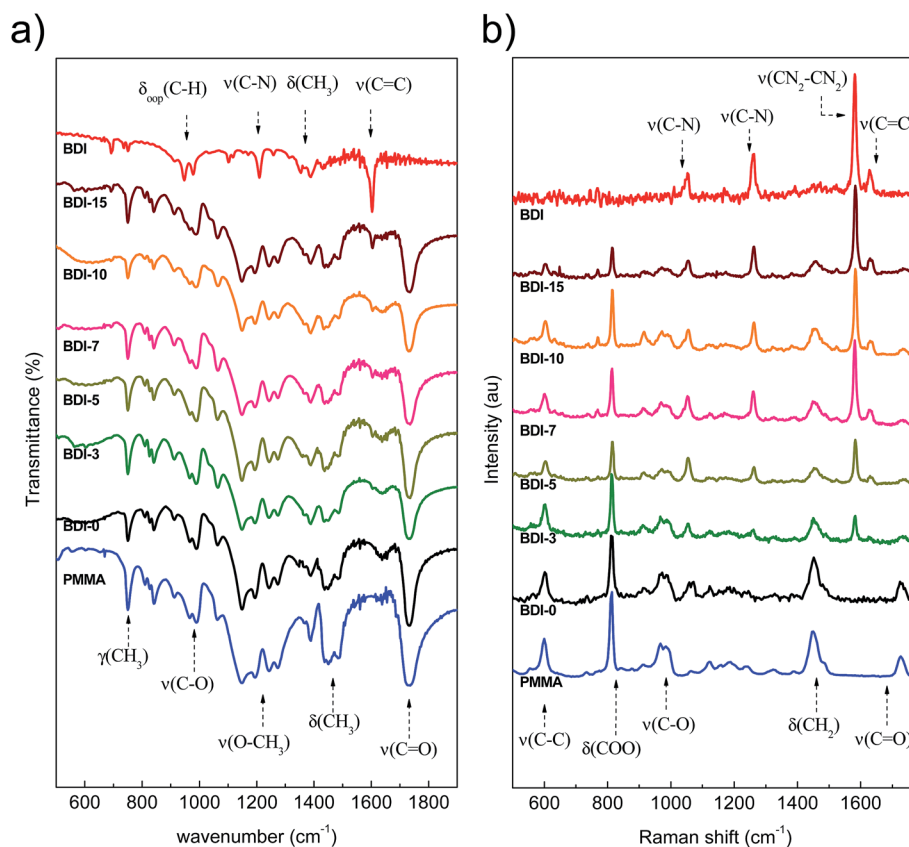


Fig. 1 FT-IR (a) and Raman (b) spectra for PMMA, BDI and BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

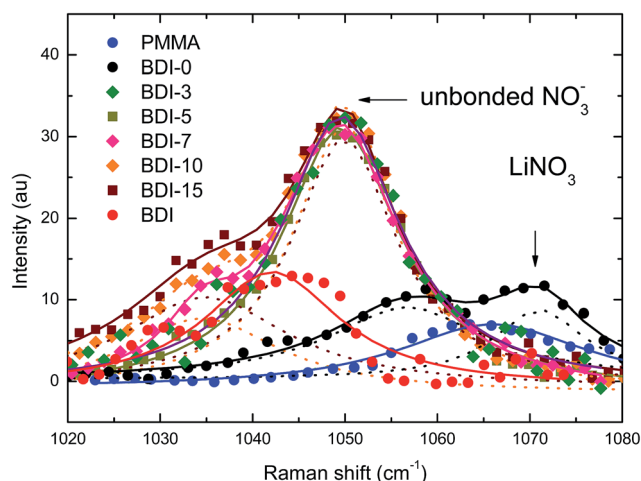


Fig. 2 Raman spectra and Lorentzian fitting for the nitrate symmetric stretching $\nu(\text{N}=\text{O})$ mode for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

Table 1 Experimental and theoretical Raman shifts for the 1000–1100 cm^{-1} region^a

	LiNO_3^{**}	BDI*	BDI-Li- NO_3^*	BDI	BDI-5
$\nu(\text{NO}_3)$	1071s	—	1040m	—	1050m
$\delta(\text{CN}_2)$	—	1037w	1028w	1042w	1035w

^a BDI and BDI-Li- NO_3 Raman shift frequencies were theoretically calculated (*) and LiNO_3 crystalline nitrate mode (**) was extracted from the literature.³⁴

the $\delta(\text{N}-\text{C}-\text{N})$ stretching, $\nu(\text{C}-\text{N})$ stretching, $\nu(\text{CN}_2-\text{CN}_2)$ stretching and $\nu(\text{C}=\text{C})$ stretching modes, respectively. All these vibrational modes were assigned using DFT theoretical simulation of the Raman spectra as described in the previous section. Samples of BDI- X with $X = 0$ – 15 exhibited a peak at $\sim 1050 \text{ cm}^{-1}$, attributed to the nitrate $\nu(\text{N}=\text{O})$ stretching mode, suggesting the dissociation of lithium from the nitrate salt, as also observed for a similar PMMA nanocomposite in our previous report.¹⁵ This nitrate stretching mode peak is expected to be located at $\sim 1070 \text{ cm}^{-1}$ for the lithium bonded

configuration of the LiNO_3 salt. The Lorentzian deconvolution of the Raman spectra in the 1020 – 1080 cm^{-1} region is shown in Fig. 2. There is evidence of nitrate dissociation for all BDI- X samples but only partial dissociation for the sample with no BDI added ($X = 0$), evidenced by the presence of two peaks at ~ 1050 and $\sim 1070 \text{ cm}^{-1}$, ascribed to the nitrate stretching mode for the non-bonded and bonded to lithium cases, respectively. On the other hand, a slight shift from ~ 1042 to $\sim 1035 \text{ cm}^{-1}$ is observed for the $\nu(\text{C}-\text{N})$ stretching mode of BDI, probably suggesting a hydrogen bonding interaction of the BDI secondary amine ($\text{N}-\text{H}$) with nitrate anions (NO_3^-) as is usually observed in these coordination compounds.^{21–23,34} Theoretical calculations of the Raman spectra for a simple model consisting of a BDI molecule, two lithium and two nitrate ions are shown in Table 1. The structure optimization shows that lithium interacts through the BDI nitrogen atom and nitrate probably interacts with BDI *via* hydrogen bonding through $\text{N}-\text{H}$, as shown in Fig. 3. The theoretical nitrate symmetric stretching mode exhibited a peak located at $\sim 1040 \text{ cm}^{-1}$, which is drastically shifted from the typically observed peak at $\sim 1070 \text{ cm}^{-1}$ for lithium nitrate.³⁵ This peak at $\sim 1040 \text{ cm}^{-1}$ was also observed in the experimental Raman spectra.

Confocal Raman images, obtained for a $75 \times 75 \mu\text{m}$ zone of the BDI- X samples ($X = 0, 3, 5, 7, 10$ and 15), are shown in Fig. 4a. The “red” zones in the confocal Raman images were obtained by filtering the BDI $\nu(\text{CN}_2-\text{CN}_2)$ stretching mode at $\sim 1583 \text{ cm}^{-1}$, while the “blue” zones were obtained by filtering the PMMA $\delta(\text{O}-\text{C}=\text{O})$ deformation mode at $\sim 817 \text{ cm}^{-1}$, revealing the presence of BDI-rich zones and PMMA-rich zones in the polymer electrolyte, respectively. The addition of BDI leads to the formation of BDI-rich zones in the polymer matrix, analogous to a polymer blend microstructure. Confocal Raman spectra, associated with the previously defined “blue” and “red” zones, are shown in Fig. 4b. The presence of unbonded nitrate, evidenced by the peak at $\sim 1050 \text{ cm}^{-1}$, is mostly observed in the BDI-rich zones, confirming that BDI shows great affinity for nitrate anions. This is probably due to the BDI interaction with nitrate anions through hydrogen bonding, suggesting that the addition of BDI leads to the decline of lithium-nitrate ionic-pair formation.

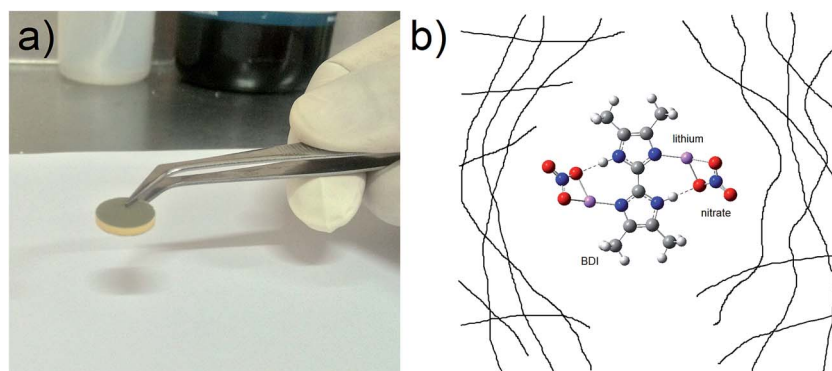


Fig. 3 (a) Photo of the solid polymer electrolyte membrane with gold blocking electrodes and (b) scheme with the proposed BDI interaction with lithium and nitrate for the BDI- X solid polymer electrolyte.

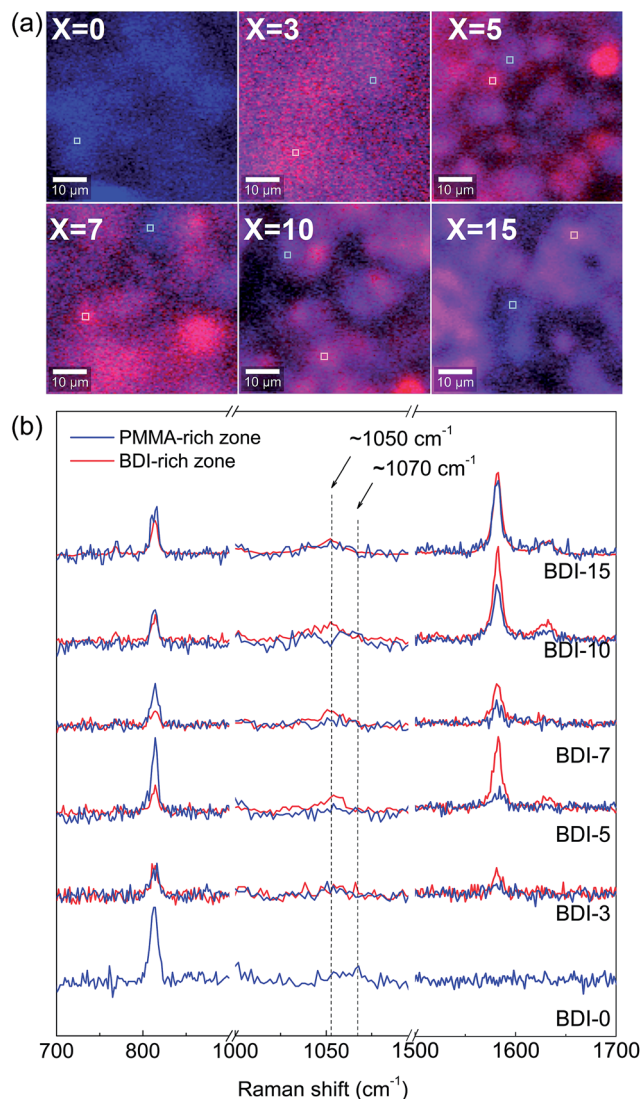


Fig. 4 (a) Confocal Raman image showing the presence of PMMA-rich (blue) and BDI-rich (red) zones for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 . The filter applied in the spectra to obtain the image was based on the intensity of the PMMA $\delta(\text{O}=\text{C}=\text{O})$ deformation at $\sim 817 \text{ cm}^{-1}$ and BDI $\nu(\text{CN}_2-\text{CN}_2)$ stretching at $\sim 1583 \text{ cm}^{-1}$, shown in blue and red, respectively. (b) Confocal Raman spectra for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 corresponding to the PMMA-rich (blue) and BDI-rich (red) zones marked in Fig. 3a. The peaks located at ~ 1070 and 1050 cm^{-1} are ascribed to the nitrate stretching mode for the cases of bonding and non-bonding with lithium, respectively.

XRD patterns for the BDI- X samples with $X = 0, 3, 5, 7, 10$ and 15 are shown in Fig. 5. In all cases, the presence of a broad peak at $2\theta \sim 15^\circ$ and two others with a lower intensity at $2\theta \sim 30^\circ$ and 43° was observed, in agreement with the typical amorphous PMMA pattern. The peak at $2\theta \sim 15^\circ$ showed a progressive shift to higher values as shown in Table 2, in relation to the decrease in the coherence length of the PMMA induced by the increasing concentration of BDI, as has also been observed for other similar PMMA composites.³⁶ The mean coherence lengths (d_1), estimated using the Bragg equation with the peak position at $2\theta_1 \sim 15\text{--}19^\circ$, are shown in Table 2. The progressive lowering of

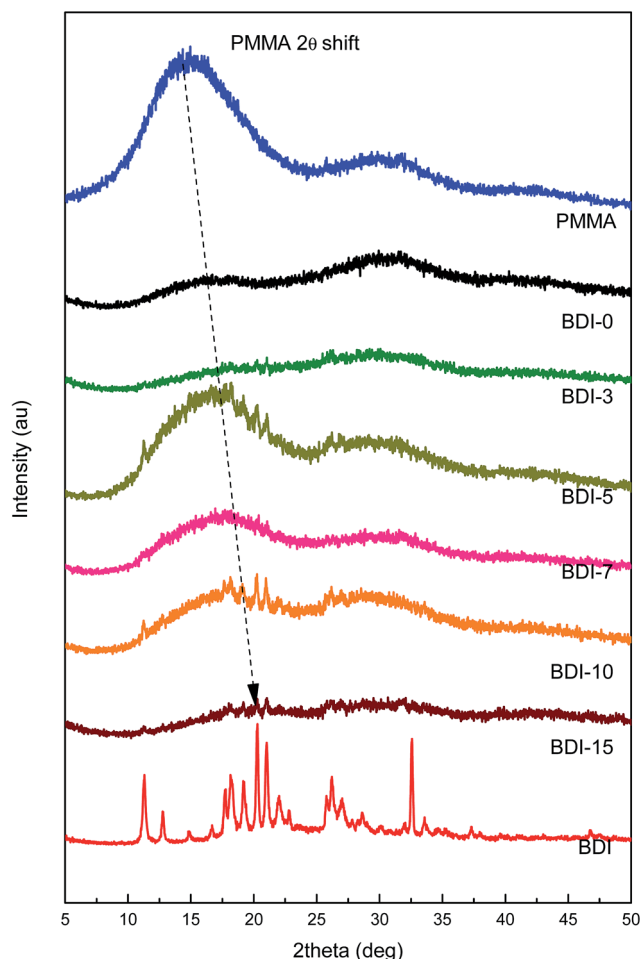


Fig. 5 XRD patterns for PMMA, BDI and BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

the mean coherence length from $d_1 \sim 0.60 \text{ nm}$ to 0.45 nm probably suggests that the mean PMMA inter-chain distances decrease with increasing concentration of BDI, similar to the typical side-chain effect observed for different acrylate and methacrylate polymers.³⁷ BDI- X with $X = 0$ and 3 showed a drastic lowering in the $2\theta \sim 15^\circ$ peak intensity, as shown in Fig. 5. This observation could be possibly attributed to the

Table 2 XRD and DSC analysis for PMMA and BDI- X with $X = 0, 3, 5, 7, 10$ and 15^a

	$2\theta_1 (^\circ)$	$d_1 (\text{nm})$	$2\theta_2 (^\circ)$	$d_2 (\text{nm})$	$T_g (^\circ\text{C})$
PMMA	15.01	0.59	30.86	0.30	~ 85
BDI-0	15.77	0.56	30.72	0.30	—
BDI-3	—	—	30.61	0.30	—
BDI-5	16.31	0.54	29.92	0.30	$\sim 50\text{--}60$
BDI-7	16.81	0.53	30.63	0.30	$\sim 50\text{--}60$
BDI-10	17.04	0.52	29.83	0.30	$\sim 50\text{--}60$
BDI-15	19.14	0.46	30.05	0.30	—

^a Mean coherence distance (d_n) was estimated from XRD data using the Bragg equation $d_i = \lambda/2\sin(\theta_i)$. Glass transition temperature (T_g) was estimated from DSC data using the linear crossover method.

polymer partial oxidation due to the presence of nitrate, which consequently leads to a drastic increase in the disorder of the PMMA chains. However, the samples where $X = 5$ and 7 showed an increase in the $2\theta \sim 15^\circ$ peak intensity, probably suggesting that BDI interacts with nitrate anions avoiding the PMMA partial decomposition, thus avoiding an increase in the disorder of the polymer chains. Nevertheless, the samples where $X = 10$ and 15 showed a progressive decrease in the peak intensity, probably due to BDI blending with the polymer chains, leading to an increase in the disorder of the PMMA chains with an increasing concentration of BDI. On the other hand, the peak at $2\theta_2 \sim 30^\circ$, associated with typical inter-monomer spacing ($d_2 \sim 0.30$ nm),³⁸ showed no drastic shift in its position for the samples of differing BDI concentration, as expected in the absence of PMMA chain cleavage or severe decomposition. The presence of low intensity peaks ascribed to the crystalline BDI reflections was also observed for BDI- X with $X = 5, 10$ and 15 , suggesting that BDI is probably partially still in a semi-crystalline form in the BDI- X polymer composites.

DSC profiles for BDI- X are shown in Fig. 6. The glass transition temperature showed a progressive decrease with increasing BDI concentration with respect to pure PMMA. Pure PMMA showed a T_g of $\sim 85^\circ\text{C}$, in accordance with the glass transition temperature of low molecular weight PMMA. The BDI- X composites showed a T_g range of ~ 50 – 60°C for the samples where $X = 5, 7$ and 10 , in agreement with a progressive increase in the disorder of the polymer chains. On the other hand, no evidence of glass transition was observed above room temperature for the samples of lower BDI concentrations ($X = 0, 3$) and for higher BDI concentrations ($X = 15$), suggesting a more pronounced increase in the disorder of the PMMA

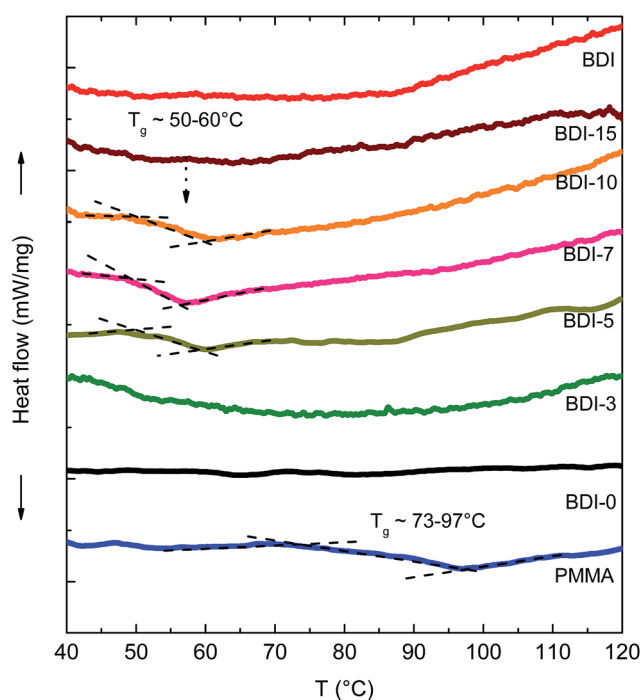


Fig. 6 DSC profiles for PMMA, BDI and BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

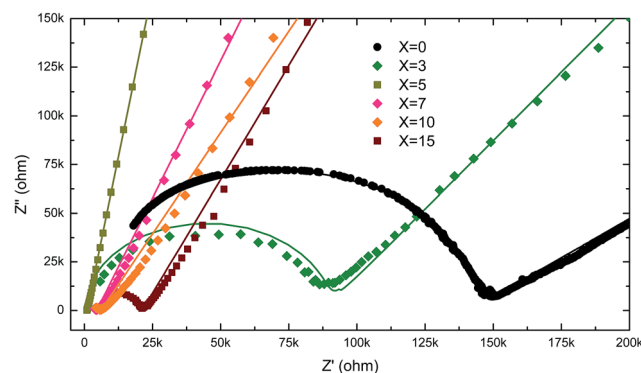


Fig. 7 Electrochemical impedance spectroscopy at $T = 20^\circ\text{C}$ for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

chains, as also evidenced by the drastic lowering of the peak intensity in the XRD pattern shown in Fig. 5.

Electrochemical impedance spectra (EIS) in the Nyquist plane form for all BDI- X composites are shown in Fig. 7. In all cases, the impedance spectra are composed of an arc circle at high frequencies related to the parallel combination of the bulk resistance (R_b) and capacitance (C). The irregularities at the electrode/electrolyte contact can be modeled using a constant phase element (CPE) connected in series with the RC parallel combination³⁹ as shown in the inset of Fig. 8. An enhancement in the lithium conductivity at room temperature was observed for all BDI- X with $X = 3, 5, 7, 10$ and 15 , with respect to $X = 0$. The total lithium conductivity for different BDI concentrations is shown in Fig. 8 and listed in Table 3, showing conductivities of $\sigma = 1.18 \times 10^{-6}, 2.01 \times 10^{-6}, 1.88 \times 10^{-4}, 3.84 \times 10^{-5}, 2.87 \times 10^{-5}$ and $8.25 \times 10^{-6} \text{ S cm}^{-1}$ for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 , respectively. The enhancement of the lithium conductivity for all BDI concentrations with respect to $X = 0$ is probably ascribed to the inhibition of the ionic-pair formation between lithium and nitrate. Based on the Raman spectroscopy analysis, we propose that BDI interacts with the nitrate anion, probably through hydrogen bonding through the N-H group, and lithium interacts through the BDI nitrogen atom, as shown in Fig. 3. The BDI- X sample with $X = 5$ showed the highest lithium

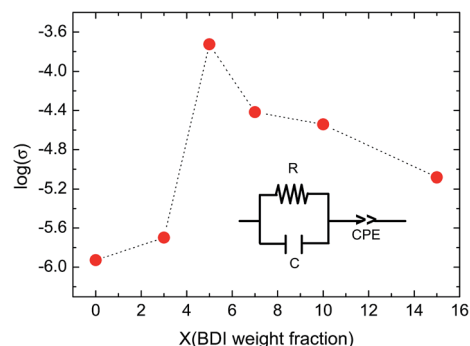


Fig. 8 Circuit model and lithium conductivity versus BDI concentration at $T = 20^\circ\text{C}$ plotted as $\log(\sigma)$ vs. X for BDI- X with $X = 0, 3, 5, 7, 10$ and 15 .

Table 3 Bulk resistance (R_b) and lithium conductivity (σ) at $T = 20^\circ\text{C}$ for BDI- X with $X = 0, 3, 5, 7, 10$ and 15^a

	R_b (kohm)	σ (S cm^{-1})
BDI-0	149.8	1.18×10^{-6}
BDI-3	88.3	2.01×10^{-6}
BDI-5	0.94	1.88×10^{-4}
BDI-7	4.606	3.84×10^{-5}
BDI-10	6.162	2.87×10^{-5}
BDI-15	21.44	8.25×10^{-6}

^a Bulk resistance (R_b) was obtained by fitting EIS data with the circuit model shown in Fig. 8 and lithium conductivity (σ) was obtained using the equation $\sigma = t/R_b A$, with the polymer electrolyte thickness (t) and the area of electrodes (A).

conductivity ($\sigma_{\text{total}} = 1.88 \times 10^{-4} \text{ S cm}^{-1}$), suggesting that this critical amount of BDI leads to an optimal relation between the nitrate bonding effect and the degree of disorder in the polymer chains. The BDI- X sample with $X = 5$ corresponds to a BDI : Li molar ratio of 1 : 2, suggesting that the optimal BDI content is the one corresponding to two lithium cations and two nitrate anions per BDI molecule, as shown in Fig. 3. However, it is also possible that both lithium and nitrate could be interacting in a molar ratio of 1 : 1 with BDI and part of the lithium is interacting with the PMMA carbonyl groups. In any case, it is important to remark that the addition of BDI leads to the decline of lithium-nitrate ion-pair formation which benefits the enhancement of lithium transport in the polymer matrix. However, independent of the BDI to lithium and nitrate ratio, the maximum lithium conductivity observed for a critical amount of BDI ($X = 5$) may also be attributed to other effects associated with the addition of BDI in the polymer microstructure. It is also important to remark that the electrolyte with no BDI ($X = 0$) exhibited a low intensity of the $2\theta \sim 15^\circ$ reflection in the XRD pattern, probably due to the partial oxidation of PMMA. On the other hand, the electrolytes with a higher loading of BDI ($X > 10$) also showed a decrease in the reflection ascribed to the PMMA inter-chain mean coherence distance, probably due to BDI blending in the PMMA matrix, leading to an increase in the mean coherence length between polymer inter-chains. However, $X = 5$ shows the highest coherence in the polymer inter-chain distances, denoted by the highest intensity of the $2\theta \sim 15^\circ$ reflection in the XRD pattern. This might suggest that low amounts of BDI prevent partial oxidation of PMMA, due to the affinity of BDI for nitrate anions. This suggests that the enhancement in the lithium conductivity is not only due to the lithium ionic-pair suppression caused by the BDI addition but it could also be related to the higher coherence of the polymer inter-chain distances. In summary, the addition of BDI shows enormous advantages in the preparation of fluorine-free solid polymer lithium-ion electrolytes such as higher chemical stability, safety and lithium conductivity.

Conclusions

In this report, we showed the effect of the addition of fluorine-free 2,2'-bis(4,5-dimethylimidazole) (BDI) in a lithium-ion solid

polymer electrolyte based on the PMMA polymer. We focused on studying the effect that the BDI addition has on the dissociation of lithium by means of confocal Raman spectroscopy. The interaction between the nitrate anion and BDI leads to a higher dissociation of lithium ions and, consequently, to the enhancement of the lithium conductivity of up to $1.88 \times 10^{-4} \text{ S cm}^{-1}$ for a 5% critical BDI concentration in these solid polymer electrolytes. XRD analysis showed that the increasing BDI concentration leads to a progressive decrease in the coherence length of PMMA chains. This analysis also showed that the critical BDI concentration of 5% does not compromise the degree of disorder in the polymer chains, leading to the highest lithium conductivity in this type of solid polymer electrolytes.

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Notes and references

- 1 J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
- 2 R. Bouchet, S. Maria, R. Meziane, A. Aboulaich, L. Lienafa, J. P. Bonnet, T. N. Phan, D. Bertin, D. Gignes and D. Devaux, *Nat. Mater.*, 2013, **12**, 452–457.
- 3 V. Di Noto, S. Lavina, G. A. Giffin, E. Negro and B. Scrosati, *Electrochim. Acta*, 2011, **57**, 4–13.
- 4 N. Shukla and A. K. Thakur, *Solid State Ionics*, 2010, **181**, 921–932.
- 5 S. Ramesh and L. Wen, *Ionics*, 2010, **16**, 255–262.
- 6 S. Panero, B. Scrosati and S. G. Greenbaum, *Electrochim. Acta*, 1992, **37**, 1533–1539.
- 7 B. Kumar and L. G. Scanlon, *J. Power Sources*, 1994, **52**, 261–268.
- 8 W. Wieczorek, A. Zalewska, D. Raducha, Z. Florjańczyk and J. R. Stevens, *J. Phys. Chem. B*, 1998, **102**, 352–360.
- 9 F. Croce, R. Curini, A. Martinelli, L. Persi, F. Ronci, B. Scrosati and R. Caminiti, *J. Phys. Chem. B*, 1999, **103**, 10632–10638.
- 10 B. Scrosati, F. Croce and L. Persi, *J. Electrochem. Soc.*, 2000, **147**, 1718–1721.
- 11 K. S. Ji, H. S. Moon, J. W. Kim and J. W. Park, *J. Power Sources*, 2003, **117**, 124–130.
- 12 J. H. Shin and S. Passerini, *J. Electrochem. Soc.*, 2004, **151**, A238–A245.
- 13 A. M. Stephan and K. S. Nahm, *Polymer*, 2006, **47**, 5952–5964.
- 14 W. Liu, N. Liu, J. Sun, P. C. Hsu, Y. Li, H. W. Lee and Y. Cui, *Nano Lett.*, 2015, **15**, 2740–2745.
- 15 M. Romero, R. Faccio, S. Vázquez and A. W. Mombrú, *Mater. Lett.*, 2016, **172**, 1–5.
- 16 L. Niedzicki, M. Kasprzyk, K. Kuziak, G. Z. Zukowska, M. Marcinek, W. Wieczorek and M. Armand, *J. Power Sources*, 2011, **196**, 1386.
- 17 L. Niedzicki, S. Grugeon, S. Laruelle, P. Judeinstein, M. Bukowska, J. Prejzner, P. Szczecinski, W. Wieczorek and M. Armand, *J. Power Sources*, 2011, **196**, 8696.

- 18 T. Trzeciak, L. Niedzicki, G. Groszek, P. Wieczorek, M. Marcinek and W. Wieczorek, *J. Power Sources*, 2014, **252**, 229–234.
- 19 L. Niedzicki, M. Kasprzyk, K. Kuziak, G. Z. Zukowska, M. Armand, M. Bukowska, M. Marcinek, P. Szczecinski and W. Wieczorek, *J. Power Sources*, 2009, **192**, 612–617.
- 20 A. Reddy Polu, H. W. Rhee and D. Kyu Kim, *J. Mater. Sci.: Mater. Electron.*, 2015, **26**, 8548–8554.
- 21 S. De Angelis Curtis, K. Kurdziel, S. Materazzi and S. Vecchio, *Thermochim. Acta*, 2010, **510**, 75–81.
- 22 M. C. Llinas, J. Farran, M. V. Capparelli, G. Anguera, D. Sanchez-Garcia, J. Teixido and S. Borros, *Tetrahedron Lett.*, 2014, **55**, 4667–4670.
- 23 A. Das, S. M. Mobin and G. Kumar Lahiri, *Dalton Trans.*, 2015, **44**, 13204–13219.
- 24 W. Kohn and L. J. Sham, *Phys. Rev. A*, 1965, **140**, 1133.
- 25 P. Hohenberg and W. Kohn, *Phys. Rev. [Sect.] B*, 1964, **136**, 864.
- 26 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 27 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 28 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671.
- 29 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283.
- 30 M. J. Frisch, *et al.*, Gaussian, Inc., Wallingford CT, 2009.
- 31 S. Ramesh, K. H. Leen, K. Kumutha and A. K. Arof, *Spectrochim. Acta, Part A*, 2007, **66**, 1237–1242.
- 32 C. P. Ennis and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14902–14915.
- 33 Suryani, C. M. Chang, Y. L. Liu and Y. M. Lee, *J. Mater. Chem.*, 2011, **21**, 7480–7486.
- 34 M. Dranka, L. Niedzicki, M. Kasprzyk, M. Marcinek, W. Wieczorek and J. Zachara, *Polyhedron*, 2013, **51**, 111–116.
- 35 R. E. Miller, R. R. Getty, K. L. Treuil and G. E. Leroi, *J. Chem. Phys.*, 1969, **51**, 1385.
- 36 S. Ramesh, C.-W. Liew and K. Ramesh, *J. Non-Cryst. Solids*, 2011, **357**, 2132–2138.
- 37 R. L. Miller, R. F. Boyer and J. Heijboer, *J. Polym. Sci., Part B: Polym. Phys.*, 1984, **22**, 2021–2041.
- 38 A. J. Christofferson, G. Yiapanis, J. M. Ren, G. G. Qiao, K. Satoh, M. Kamigaitoc and I. Yarovsky, *Chem. Sci.*, 2015, **6**, 1370–1378.
- 39 R. J. Sengwa, P. Dhatarwal and S. Choudhary, *Electrochim. Acta*, 2014, **142**, 359–370.