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POLYMER IONIC LIQUID BEARING RADICALS AS AN ACTIVE MATERIAL FOR ORGANIC BATTERIES WITH ULTRAFAST CHARGE-DISCHARGE RATE

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Abstract

We report on the synthesis of a new polymer ionic liquid (PIL) based on polyvinylimidazolium bearing a pendent nitroxide radical on each monomer unit. Firstly, the quaternization of 1-vinylimidazole by a brominated alkoxyamine, *i.e.* a protected tetramethylpiperidinyloxy (TEMPO) nitroxide, was achieved. Then, the bromide anion was substituted by anion exchange reaction for the bis(trifluoro-methanesulfonyl)imide (TFSI) anion. The as-obtained monomer was successfully polymerized by free radical polymerization at low temperature (40°C) by using 2,2'-azobis(4-methoxy-2.4-dimethyl valeronitrile) as initiator. Finally, the C–O bond of the alkoxyamine pendant groups was thermally cleaved releasing the redox-active TEMPO nitroxide radicals. The PIL bearing TEMPO groups was coated onto a carbon nanotubes buckypaper and tested as cathode in a lithium ion battery. Such battery remarkably exhibits a high charge/discharge rate capability, e.g. at 60C the full charge is reached in 1min and a high cycling stability; 100% of the initial capacity 60mAh/g is kept after 1300 cycles.

Keywords : Polymer ionic liquids, TEMPO, Organic radical batteries, Polyvinylimidazolium

1. Introduction

Polymers bearing nitroxide radicals are widely studied as electrode-active materials in rechargeable organic radical batteries (ORB) because they exhibit a good electrochemical stability, a long cycle stability and a high flexibility [1–4]. Thanks to its rapid charge-transfer process and high diffusion coefficient, the poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate) (PTMA) is one of the most studied polymer bearing TEMPO-radical groups [5–10]. Due to its electrically insulating nature, PTMA was generally combined with conductive nanofillers including activated carbon [11,12], super P [13], carbon black [14], graphene [15–17], and multiwall carbon nanotubes (MWNTs) [18–21] to increase the electronic conductivity of the PTMA electrode. In a recent work, some of us have reported MWNTs buckypaper electrodes uniformly and strongly electrografted with PTMA for use as ORB cathodes [22]. This ORB cathode configuration with a radical polymer uniformly coating the highly conducting

3DMWNTs network, presents an efficient counter-ion penetration and a quantitative and fast charge propagation during the charge-discharge process [23].

Beside, due to their unique properties, ILs have been investigated as potential conducting electrolytes for electrochemical devices including lithium ion batteries [24–26], supercapacitor, fuel cells [27], and solar cells [28,29]. In 2008, Lee et al proposed IL based on imidazolium hexafluorophosphate bearing TEMPO-radical as cathode-active materials in lithium secondary batteries with sufficient ionic conductivity to ensure high charge transfer level at fast reaction condition [24]. The obtained ORB cathode exhibits high cycling performances at 1 and 10C-rate. However, at high rate (20C) ILs-TEMPO showed capacity degradation after 50 cycles. The partial dissolution of ILs-TEMPO small molecules in various organic solvents, including carbonate-based battery electrolytes, leads to diffusion inside the battery and to self-discharging problems at long term. Recently, Mecerreyes et al reported polymer ionic liquids (PILs) with redox-active counter-ions (anthraquinone and TEMPO) as active materials in different energy storage technologies [30]. Anthraquinone based PILs tested as electrode active materials in LIBs exhibit a moderate initial capacity of 85mAh/g which decreases gradually after a few cycles. This low cycling stability is related to the partial dissolution of the anthraquinone counter-ions in the electrolyte.

With the objective to prevent the dissolution and/or diffusion of the redox-active group in the electrolyte and thus improve the cycling performances and rate capability of batteries, we aimed to develop a polymer ionic liquid (PIL) with redox-active groups chemically anchored to the PIL backbone. Therefore, we developed a synthesis method to prepare a polyvinylimidazolium polymer bearing a pendent TEMPO unit on each imidazole unit (Scheme 1). When this innovative polymer is homogeneously coated on buckypaper-MWNTs, it behaves as an efficient material for ORB cathode. Indeed, the excellent ionic conductivity of the PIL and the ultra-rapid TEMPO redox moieties combined with the MWNTs electron conductor 3D-network insure an efficient and rapid counter-ions diffusion and electrons transport, allowing quantitative charging-discharging capacity at high current density and long cycling stability.

2. Experimental section

2.1. MATERIALS

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99%, ABCR), bromoacetyl bromide (98%, TCI). 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxy (H-TEMPO) (98%, TCI), 2,2’-Azobis (4methoxy-2, 4-dimethylvaleronitrile) (V70) and all other reagents were purchased from Sigma Aldrich. 1-(1-Phenylethoxy)-2,2,6,6-tetramethylpiperidin-4-ol) (pTEMPO-OH) and 4-acryloyloxy-1-((1’-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (pTEMPO-Acry) were synthesized as described in the previous work [31]. Poly(TEMPO-Acry) (M_n: 22.000g/mol) and poly(N-Vinyl-3-ethylimidazolium)-bis(trifluoro-methanesulfonyl)imide) (poly(ethyl-VImTFSI)) (M_n: 10.000g/mol) were synthesized as reported in the literature [32–34]. The solvents were purchased from VWR with the highest purity available and used as received without further purification. MWNTs (average outer diameter 10nm, purity higher than 95wt%, oxygen content 7%) were supplied by Nanocyl S.A.

2.2. SYNTHESIS OF THE BROMINATED PROTECTED-TEMPO (PTEMPO-BR): *I.E.* 2,2,6,6-TETRAMETHYL-1-(1-PHENYLETHOXY)PIPERIDIN-4-YL 2-BROMOACETATE

To a solution of 5.25g (19mmol) of pTEMPO-OH and 3g (19mmol) of bipyridine in dichloromethane (70mL), bromoacetyl bromide 3.28mL (38mmol) in dichloromethane (30mL) was slowly added under argon. The mixture was stirred in the cooling bath for 1h and then was standing overnight at room temperature. The precipitate was removed by filtration and the filtrate was washed with 10% NaOH, then dilute HCl (2.0M) and finally distilled water (30mL). The solution was dried over $MgSO_4$ and was purified by flash column chromatography using (9:1, hexane/THF) as solvent to afford 5g of yellow oil (yield =66%).

^{1}H NMR (DMSO-d_6) δ: 7.37–7.17 (m, 5H), 5.11–4.96(m, 1H), 4.78(q, 1H, J = 5.58 Hz), 4.31(q, 1H, J =5.74 Hz), 1.97–1.83 (m, 2H), 1.80 (d, 3H, J =5.78 Hz), 1.70–1.54 (m, 2H), 1.49 (d, 3H, J =5.48 Hz), 1.35 (s, 3H), 1.27 (s, 3H), 1.13(s, 3H), 0.68(s, 3H).

2.3. SYNTHESIS OF THE PROTECTED-TEMPO ANCHORED VINYL IMIDAZOLIUM MONOMER, BROMIDE SALT (PTEMPO-VIMBR): *I.E.* 3-(2-OXO-2-((2,2,6,6TETRAMETHYL-1-(1-PHENYLETHOXY)PIPERIDIN-4-YL)OXY)ETHYL)-1VINYLIMIDAZOLIUM BROMIDE

under stirring, 5g (12.6mmol) of **pTEMPO-Br** was slowly added to a solution of 1.77g (19mmol) of 1-vinylimidazole in 5mL of methanol. The mixture was stirred at 40°C for 24h. After cooling to room temperature, 100mL ether was added to the mixture causing precipitation of the monomer as a white solid. This solid was recovered by filtration and purified by recrystallization in acetonitrile. The yield was 85% (5.26g).

^{1}H NMR (250MHz, DMSO-d_6) δ 9.54 (s, 1H), 8.28 (s, 1H), 7.90 (s, 1H), 7.43 (dd, J = 15.6, 8.7 Hz, 1H), 7.29 (m, 5H), 6.01 (dd, J =15.7, 2.5 Hz, 1H), 5.45 (dd, J =8.8, 2.5 Hz, 1H), 5.29 (s, 2H), 5.00 (m, 1H), 4.74 (q, J = 6.6 Hz, 1H), 1.90 (d, J = 11.9 Hz, 1H), 1.77 (dt, J = 12.6, 3.7 Hz, 1H), 1.54 (dd, J =22.3, 10.4 Hz, 2H), 1.41 (d, J =6.4 Hz, 3H), 1.30 (s, 3H), 1.18 (s, 3H), 1.03 (s, 3H), 0.60 (s, 3H).

2.4. SYNTHESIS OF THE PROTECTED-TEMPO ANCHORED VINYL IMIDAZOLIUM MONOMER, TFSI SALT (PTEMPO-VIMTFSI): *I.E.* 3-(2-OXO-2-((2,2,6,6TETRAMETHYL-1-(1-PHENYLETHOXY)PIPERIDIN-4-YL)OXY)ETHYL)-1VINYLIMIDAZOLIUM BIS(TRIFLUOROMETHANESULFONYL)IMIDE

pTEMPO-VImBr (2g, 4.07mmol) was dissolved in 15mL of methanol and slowly added dropwise to an aqueous solution of LiTFSI (2.35g, 8.1mmol) in deionized water. Methanol was removed under reduced pressure, the targeted pTEMPO-VImTFSI salt was extracted with ethyl acetate and was washed with deionized water five times to remove LiBr and excess of LiTFSI salts. The complete removal of the bromide ions was checked by adding a $AgNO_3$ solution (0.1mol/L) to the aqueous extracts. The organic phase was dried over anhydrous $MgSO_4$, and solvent was removed first by rotary evaporator, then under oil pump for 12h at room temperature to obtain a light yellow oil. (yield 93%).

^{1}H NMR (250 MHz, DMSO-d_6) δ 9.40 (s, 1H), 8.23 (s, 1H), 7.86 (s, 1H), 7.48–7.36 (dd, J = 15.6, 8.7 Hz, 1H), 7.35 (m, 5H), 5.99 (dd, J =15.6, 2.5 Hz, 1H), 5.47 (dd, J =8.7, 2.5 Hz, 1H), 5.23 (s, 2H), 5.00 (m, 1H),

4.76 (q, *J* =6.7 Hz, 1H), 1.91 (d, J =12.1 Hz, 1H), 1.78 (d, *J* = 12.4 Hz, 1H), 1.59 (dd, *J* = 22.3, 10.4 Hz, 2H), 1.43 (d, *J* =6.5 Hz, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 1.05 (s, 3H), 0.63 (s, 3H).

2.5. POLYMERIZATION OF THE PROTECTED TEMPO ANCHORED VINYL IMIDAZOLIUM MONOMER (POLY(PTEMPO-VIMTFSI)): *I.E.* POLY(3-(2-OXO-2-((2,2,6,6TETRAMETHYL-1-(1-PHENYLETHOXY) PIPERIDIN-4-YL)OXY)ETHYL)-1-VINYLIMIDAZOLIUM BIS(TRIFLUOROMETHANESULFONYL)IMIDE)

In a typical polymerization experiment, **pTEMPO-VImTFSI** monomer (1g) and dry DMF (5mL) were purged with N_2 for 30min and V70 (2 wt%) was added to the solution, then the reaction mixture was degassed by three freeze-pumpthaw cycles and stirred in an oil bath at 40°C for 16h. The monomer conversion (75%) was determined by ^{1}H NMR spectroscopy in DMSO-d_6. After polymerization, the polymer was purified by dialysis in ethanol to remove the monomer, then the polymer was precipitated in water and dried under vacuum at 40°C. Macromolecular parameters (M_w, M_w/M_n) were determined by SEC in THF/LiTFSI solution (10mM) vs. PS standards.

2.6. DEPROTECTION OF THE TEMPO MOIETIES TO PRODUCE THE TARGETED RADICALANCHORED POLYMERS (POLY(TEMPO-VIMTFSI))

A solution of poly(pTEMPO-VImTFSI) in tert-butylbenzene (0.01 gml^{-1}) was heated at 135°C in the presence of oxygen for 12h. After deprotection the resulting polymer was no more soluble in tertbutylbenzene and was thus collected easily by filtration. For purification, the polymer was dissolved in a minimum of dichloromethane and precipitated in diethyl ether. After drying under vacuum at 40°C, the final targeted polymer poly(TEMPO-VImTFSI) was recovered as a brown solid (85% of yield). Macromolecular parameters (M_w, M_w/M_n) were determined by SEC in THF/LiTFSI solution (10mM) vs. PS standards.

2.7. PREPARATION OF THE POLY(TEMPO-VIMTFSI)-MWNTS BUCKYPAPER

MWNTs (10mg) and poly(TEMPO-VImTFSI) (10mg) were dispersed in acetonitrile (20mL) using at typical bath sonicator (power = 100w, frequency =42kHz) for 2h. The solution was filtered onto a nylon filter with a Millipore filtration hardware, leading to the formation of a PIL/MWNTs buckypaper composite. Poly(TEMPOVImTFSI)/MWNTs buckypaper composite is first dried in ambient air at room temperature for 2h, then at 60°C under vacuum for 24h. The resulting material is then cut into discs (1.2cm diameter, total weight of 2.0mg each) for electrochemical measurements.

2.8. PREPARATION OF THE POLY(ETHYL-VIMTFSI)-MWNTS AND POLY(TEMPO-ACRY)-MWNTS BUCKYPAPERS

poly(ethyl-VImTFSI)/MWNTs and poly(TEMPO-Acry)/MWNTs buckypapers were prepared by using the same procedure as described for poly(TEMPO-VImTFSI)-MWNTs. The amount of active polymer (poly(TEMPO-Acry)) (20mg) was doubled as compared to the MWNTs (10mg) due to the low interaction of the polyacrylic backbone with the MWNTs.

2.9. CHARACTERIZATION

^{1}H NMR spectra of the synthesized materials were recorded on a Bruker advance 250MHz spectrometer using DMSO-d_6 as solvent. FTIRATR spectra were recorded with a thermofisher ATR instrument in the 4000–600 cm^{-1} range. Thermal behavior was determined using a thermogravimetric Analyzer TGA, Q500 from TA instruments, at a heating rate of 10°C min^{-1} within the range of 25–600°C. Macromolecular parameters of the polymers (M_n, M_w/M_n) were determined by size exclusion chromatography (SEC), with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer detector 2000, carried out in tetrahydrofuran (THF) containing 10mM LiTFSI (flow rate: 1mL min^{-1}) at 35°C. PSS SDV analytical linear S 5µm column (molar mass range: 100–150,000Da) and protected by a PL gel 5µm guard column, was calibrated with PS standard (580–467,000g/mol). Scanning electron microscopy (SEM; JEOL JSM 840-A) were recorded after metallization with Pt (30nm). Transmission electron microscopy images were recorded with a Philips CM100 equipment.

2.10. ELECTROCHEMICAL MEASUREMENTS

Cyclic voltammetry measurements (CV) and galvanostatic charge-discharge (Battery tests) were performed with a Bio-logic VMP3 multichannel potentiostat using Coin cells (CR2032) and assembled in an Ar-filled glove box (MBraun). The resulting poly(TEMPOVImTFSI)/MWNTs buckypaper was used as working electrode and lithium metal foil as anode in a coin cell battery. A Celgard separator soaked with 100µl of LP71 (1 M LiTFSI in EC:DEC:DMC 1:1:1) electrolyte. Charge-discharge curves were recorded at different current density between 2.0 and 3.8V (vs. Li/Li$^+$).

3. Results and discussion

The investigated strategy to synthesize the targeted poly(vinylimidazolium) bearing covalently anchored TEMPO radicals is shown in scheme 1. The starting product is the hydroxy-alkoxyamine 3-(2-oxo-2((2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidin-4-ol (pTEMPO-OH), which was synthesized as reported in our previous works [31]. Indeed, due to their high reactivity with radicals, the protection of the TEMPO radical in alkoxyamine is necessary to avoid termination reactions during the radical polymerization of their corresponding vinylimidazolium monomer. As presented in scheme 1, the esterification of this hydroxy-alkoxyamine with bromoacetyl bromide gives a brominated derivative (pTEMPO-Br) (^{1}H NMR spectrum presented in Fig. S1) suitable for the quaternization reaction of N-vinyl imidazole to give the Nvinyl imidazolium monomer bearing the protected TEMPO (pTEMPOVIm-Br). Finally, to obtain the desired monomer (pTEMPO-VImTFSI) an anionic exchange reaction is performed with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) to substitute bromide ion with TFSI. Indeed, ionic liquids with a TFSI counter-anion are preferred due to a broader electrochemical stability window and a higher dissociation of the ion pairs compared to the corresponding halide [33,34]. The chemical structure and purity of the pTEMPO-VImTFSI monomer was confirmed by ^{1}H NMR spectroscopy (Fig. 1). The anion exchange was confirmed, on one side, by the complete removal of the bromide residue by the treatment with a silver nitrate solution and on the other side, by FTIR analysis. The ATR/FTIR spectrum of pTEMPO-VImTFSI (Fig. S2) reveals the characteristic bands of the TFSI$^-$ counter-ions assigned to the CF_3 groups (at 1175 cm^{-1}), to the SO_2 function (stretching: $\nu_a SO_2$ at 1348 cm^{-1}, $\nu_s SO_2$ at 1135 cm^{-1} and bending: $\delta_a SO_2$ at 612 cm^{-1}), to the S−N−S group (stretching: ν_a at

1050 cm^{-1}, ν_s at 765 cm^{-1}) and to the C–S bonds (at 790 cm^{-1}). Polymerization of this monomer was performed in DMF by free radical polymerization at 40°C using V70 as initiator ([Monomer]/[V70] = 50/1). At this temperature, the alkoxyamine remains stable enough to avoid interference with the free-radical process. After 16h of polymerization, 75% of conversion is reached and the obtained polymer was purified by precipitation in diethylether and dialyzed in methanol. SEC analysis in THF (Fig. S3) confirms the formation of polymer chains with an apparent low molecular weight (M_w= 13700g/mol toward PS standard) and a relatively narrow dispersity (M_w/M_n= 1.58). ^{1}H NMR spectrum confirmed the structure of the poly(pTEMPO-VImTFSI) (Fig. 1). The last step to reach the targeted poly(TEMPO-VImTFSI) consists in the deprotection of the TEMPO radicals by cleavage of the alkoxyamine at 135°C in presence of O_2 [35,36]. The used conditions were already well described in a previous paper for the deprotection of the same alkoxyamine on an acrylic backbone for which a yield of the radical production was about 90% [31]. After deprotection, the SEC trace shows a shift toward lower elution volume corresponding to an apparent molecular weight for the deprotected polymer of M_w=12500g/mol (M_w/M_n= 1.64) (Fig. S3).

The thermal stability of the final poly(TEMPO-VImTFSI) polymer was investigated by thermogravimetric analysis (TGA) under N_2 atmosphere. As shown in Fig. S4, poly(TEMPO-VImTFSI) exhibits a good thermal stability with a minor degradation at 250°C (with 15% weight loss) and main degradation at 400°C. This result confirms that the thermal properties of poly(TEMPO-VImTFSI) are suitable for use over the wide temperature ranges that are generally encountered in batteries applications.

Non-covalent functionalization of pristine multi-wall carbon nanotubes (MWNTs) with poly(TEMPO-VImTFSI) has been carried out by mixing the MWNTs in a solution of the polymer in acetonitrile under ultrasonication for 2h. The imidazolium-based ionic liquids which possess a very high dielectric constant, can effectively shield the strong π–π stacking interactions between MWNTs and thus efficiently disperse them [37–39]. After standing for one day, a very stable suspension of PILs functionalized MWNTs was observed, while large agglomerates are observed on the dispersion of pristine MWNTs in pure acetonitrile (Fig. S5). TEM analysis of the functionalized MWNTs with poly(TEMPOVImTFSI) (poly(TEMPO-VImTFSI)-MWNTs) drop-cast from acetonitrile dispersion on a copper TEM grid shows individualized MWNTs, in sharp contrast to densely entangled pristine MWNTs (Fig. 2a and b). This confirms that the poly(TEMPO-VImTFSI) is able to interact homogeneously with the MWNTs reducing their entanglements and bundles. Vacuum filtration of these poly(TEMPO-VImTFSI)/MWNTs dispersions allowed us to recover them as a buckypaper. After several washings in order to remove the non-adsorbed polymer, the amount of polymer in the buckypaper was determined by TGA under N_2 atmosphere. As observed from the TGA profiles (Fig. S6), the poly(TEMPO-VImTFSI)MWNTs buckypaper contains 15% of polymer. The buckypaper morphology was analysed by SEM (Fig. 2c and d) that clearly shows the homogeneous coating of the MWNTs by the polymer guaranteeing good contact between the active material and the current collector, which is an important parameter for electrochemical performance.

The electrochemical performance of this new redox active PIL was tested using a binder-free flexible Buckypaper as current collector which is prepared using a highly conductive MWNTs. The redox activity of poly(TEMPO-VImTFSI) was examined first by cyclic voltammetry (CV). Fig. 3 shows the representative CV curves for the poly(TEMPOVImTFSI)-MWNTs composite electrode at room temperature between 2 and 4V vs Li/Li^+ at a scan rate of 5mV/s. The first cyclic voltammogram of poly(TEMPO-VImTFSI)-MWNTs composite displays two irreversible oxidation peaks at 2.8V and 3.3V

that are decreased or completely disappeared in the following scans. These peaks could correspond to oxidation of MWNTs and/or impurities present at the first cycle. More interestingly, a clearly reversible redox wave is visible at 3.6V vs Li/Li^+ related to the nitroxide/oxoammonium couple. The cathodic to anodic peak separation is observed with a symmetric and narrow peak-to-peak separation (ΔE 95mV), suggesting a rapid diffusion of the lithium and the counter-ion through the composite. After three successive anodic and cathodic waves, the poly(TEMPOVImTFSI)-MWNTs electrode presents a stable redox activity, indicating the good oxidation/reduction reversibility of poly(TEMPO-VImTFSI).

In order to characterize the electrochemical properties of poly (TEMPO-VImTFSI), half-cells with poly(TEMPO-VImTFSI)-MWNTs as working electrode, lithium plate as the counter electrode and LiTFSI as electrolyte were fabricated. The electrochemical performances of poly (TEMPO-VImTFSI) were measured by galvanostatic charge/discharge experiments in the potential range from 2 to 3.8V (Vs Li/Li^+) at 1C. The charging and discharging curves of the poly(TEMPO-VImTFSI)MWNTs exhibited a plateau voltage at 3.62V (Fig. S7), which is in agreement with the redox potential of the pendant TEMPO groups of the polymer.

Fig. 4a shows the charge/discharge capacity and cycling performances of poly(TEMPO-VImTFSI) at a rate of 1C (1C = 45mA/g). The poly(TEMPO-VImTFSI) based cathode exhibits a high initial charge capacity of 170mAh/g which decreases to 88mAh/g after 20 cycles and stabilizes at 78mAh/g after 100 cycles, which is 74% higher than the theoretical capacity of poly(TEMPO-VImTFSI) (45mAh/g). In order to elucidate the origin of this excess capacity, a second buckypaper poly (ethyl-VImTFSI)-MWNTs was prepared by mixing MWNTs and a PIL polymer that does not bear the TEMPO groups, *i.e.* (Poly(N-Vinyl-3ethylimidazolium)-bis(trifluoro-methanesulfonyl)imide) (poly(ethylVImTFSI)). This poly(ethyl-VImTFSI)-MWNTs cathode delivers a stable reversible charge/discharge capacity after 100 cycles (36mAh/g) attributed to electric double layer capacitance (EDLC) of the buckypaper [40]. We can conclude that the capacity of poly(TEMPO-VImTFSI)MWNTs is related to the faradic contribution of TEMPO-redox groups of the poly(TEMPO-VImTFSI) and EDLC contribution of poly(TEMPOVImTFSI)-MWNTs based-buckypaper.

Fig. 4b shows the power performances of poly(TEMPO-VImTFSI)MWNTs at different current density ranging from 1C to 60C and excellent rate performances with charge capacity of 78, 77, 75, 73, 70 and 57mAh/g at current density of 1C, 2C, 4C, 10C, 20C and 60C, respectively. In parallel, the rate performances of MWNTs buckypaper at different current density ranging from 1C to 60C was investigated (Fig. S8). As it can be noticed, the pristine MWNTs buckypaper cathode delivers an initial discharge capacity of 40mAh/g at 1C and decreases drastically with increasing the current density showing that the contribution of EDLC to the power performances becomes negligible (0.02mAh/g) at 60C. The very low capacity of the MWNTs at high C-Rate evidences the preponderant role of the redox-active poly(TEMPOVImTFSI) in the capacity performances of the composite electrode.

To understand the specific contribution of the ionic group to the performances of poly(TEMPO-VImTFSI), a polymer bearing the redoxactive TEMPO attached to an acrylate backbone, *i.e.* poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylate) (poly(TEMPO-Acry)) was synthesized (Fig. S9) and compared to poly(TEMPO-VImTFSI) [22]. Fig. 4c clearly evidences a high rate capability of poly(TEMPO-VImTFSI)MWNTs electrode allowing fast charging and discharging at high current density without loss of the charge-discharge capacity, which is superior compared to poly(TEMPO-Acry)-MWNTs. Even at high C-rate 60C, poly(TEMPO-VImTFSI)/MWNTs registered 57mAh/g (27% capacity retention), while, poly(TEMPO-Acry)/MWNTs at the same C-rate registered 51mAh/g (49% capacity retention). Fig. 4d

presents the long cycling stability of poly(TEMPO-VImTFSI)/MWNTs electrode at 60C and shows excellent cycling stability with retention of 100% of initial charge capacity and superior coulombic efficiency after 1300 cycles. The good rate performance and the cycling stability of poly(TEMPOVImTFSI)-MWNTs paper composite confirm the beneficial effect of PILs supported TEMPO radicals associated with MWNTs in buckypaper configuration which increases ions and electrons transport. Compared to the poly(TEMPO-Acry) based electrode, PILs-supported TEMPO radical show higher retention of initial capacity and high cycling stability at high current density.

4. Conclusion

In summary, we demonstrated the successful synthesis of the TEMPO-anchored PIL via free radical polymerization of the alkoxyamine-anchored vinyl imidazolium monomer at low temperature followed by the deprotection of the TEMPO radicals. The MWNTs buckypaper coated by this TEMPO-anchored PIL is advantageously used as cathode material for batteries that exhibit a good charge-discharge capacity at high current density and long cycling stability. After 1300 cycles, poly(TEMPO-VImTFSI)-MWNTs maintains 100% of the initial charge capacity (60mAh/g) at 5A/g of current density. These remarkable electrochemical properties can be related to the covalent combination of PIL and TEMPO radicals in the same polymer which insures high ions rate diffusion and high affinity with the electrolyte solution. The highly conductive MWNT buckypaper guarantees the rapid electron transfer. The improved performances of this novel IL-containing polymer as compared to PTMA without IL were evidenced in half-cells containing carbonate electrolyte able to swell these polymers. By using solid electrolyte, an even larger beneficial effect of the IL-segment could be expected. Therefore, this innovative PIL bearing radicals shows a great potential for fabricating flexible organic batteries with high performances and ultrafast charge/discharge rate.

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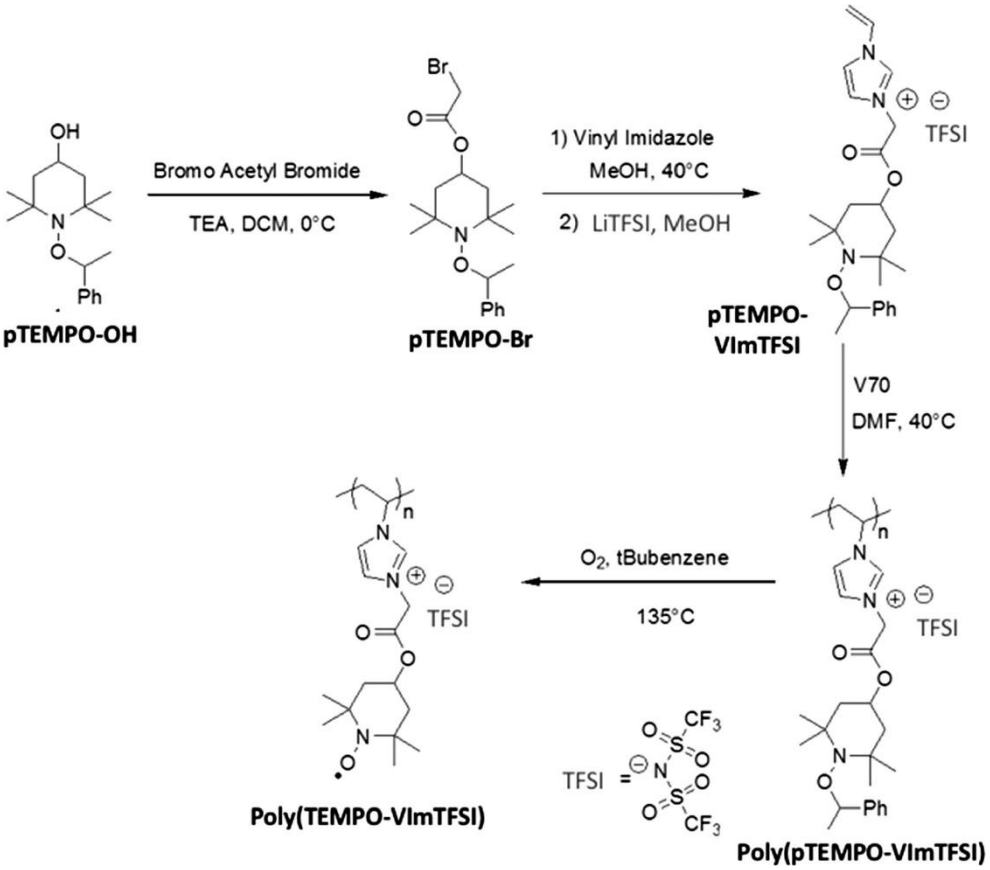
Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.eurpolymj.2018.07.028.

5. Scheme

Scheme 1. *Synthesis procedure of the polymer ionic liquid bearing nitroxide free-radicals.*



6. Figures

Fig. 1. *^{1}H NMR spectrum in DMSO-d_6 of monomer pTEMPO-VImTFSI and the corresponding polymer poly(pTEMPO-VImTFSI).*

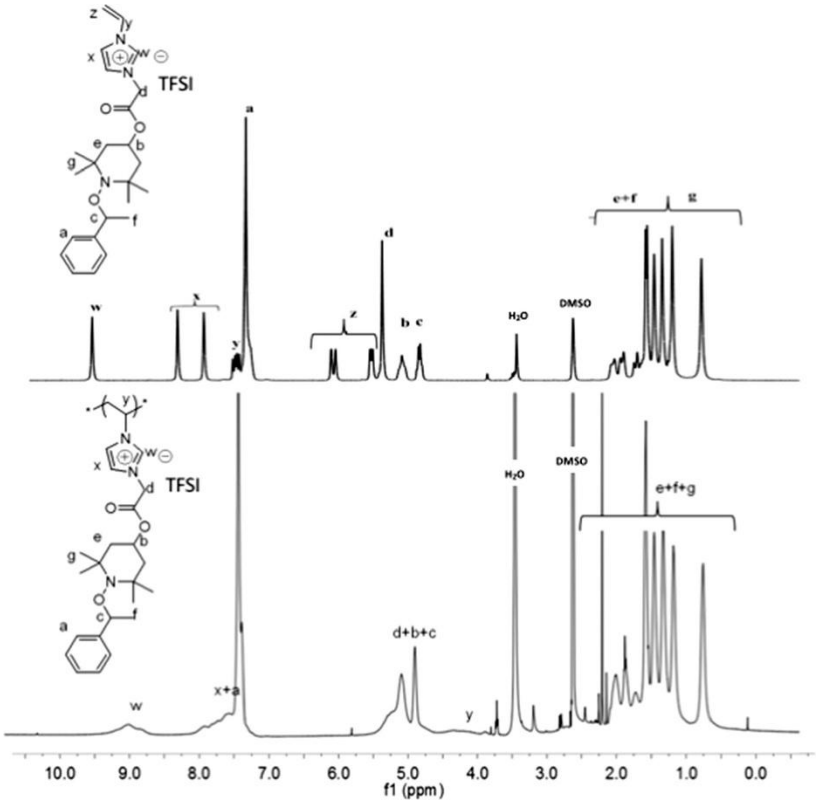


Fig. 2. *Transmission electron microscopy images of (a) pristine MWNTs and (b) poly(TEMPO-VImTFSI)-MWNTs. Scanning electron microscopy images of (c) MWNTs Buckypaper and (d) poly(TEMPO-VImTFSI)-MWNTs buckypaper with 15% of polymer.*

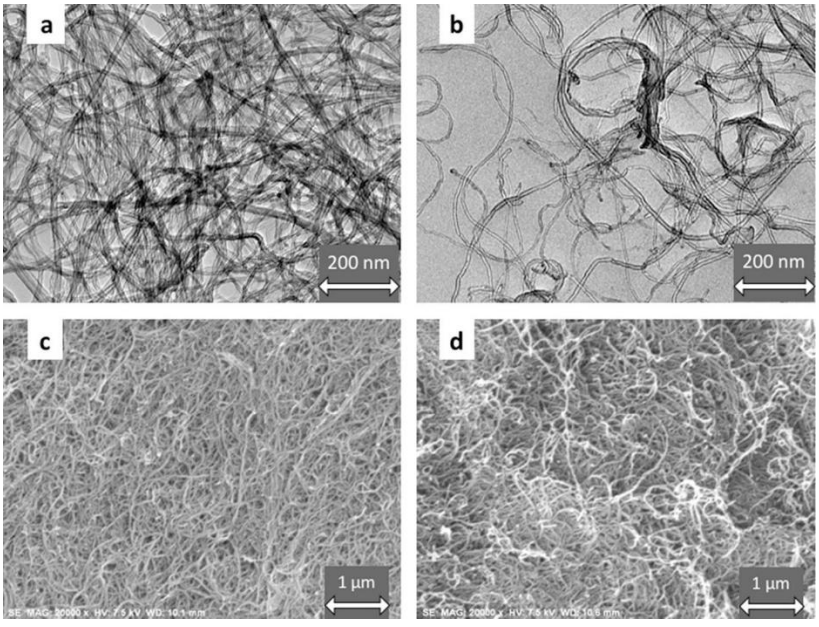


Fig. 3. *Cyclic voltammograms of poly(TEMPO-VImTFSI)-MWNTs buckypaper between 2 and 4V vs Li/Li$^+$ at a scan rate of 5mV/s.*

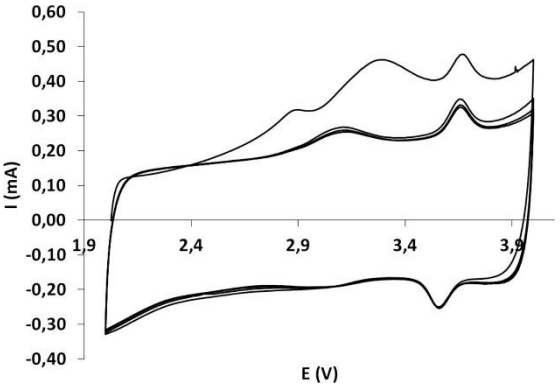
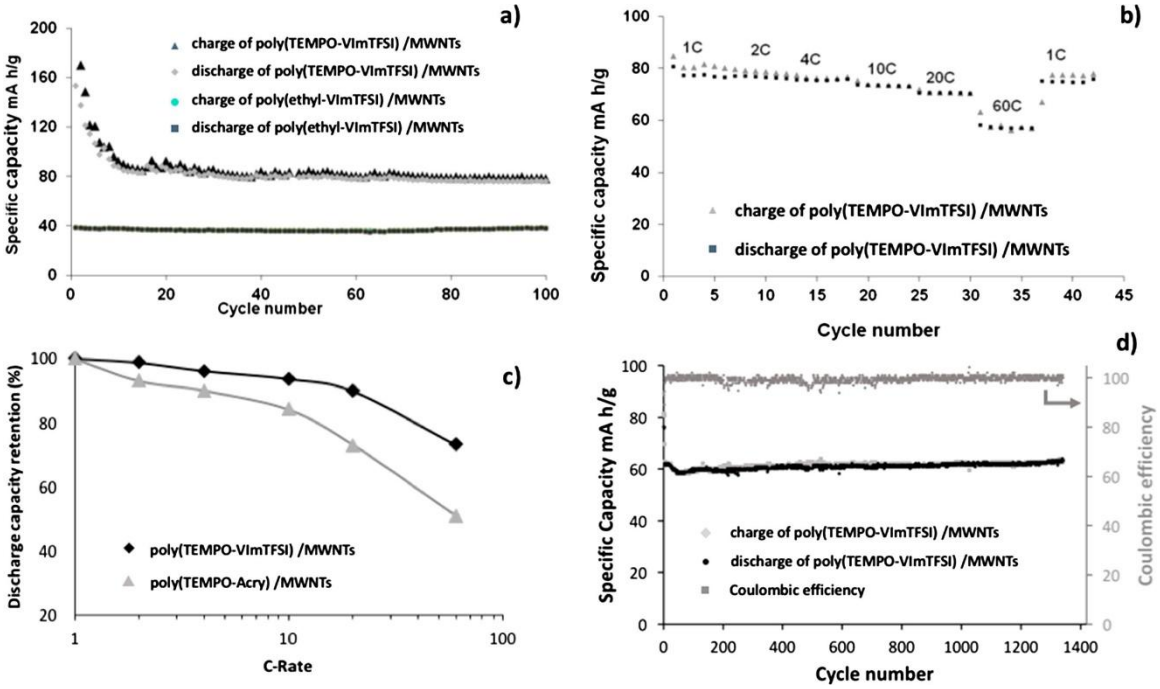


Fig. 4. *(a) Cycling performances of poly(TEMPO-VImTFSI)-MWNTs and poly(ethyl-VImTFSI)-MWNTs cathode at 1C (b) rate performances of poly(TEMPO-VImTFSI)-MWNTs cathode between 1C and 60C (c) Modified Peukert plots, indicating retention of discharge capacity of poly(TEMPO-VImTFSI)-MWNTs and poly(TEMPO-Acry)-MWNTs as a function of C rate in logarithmic scale (Capacity at different C rate are normalized with respect to the capacity at 1C) (d) long cycling stability of poly(TEMPO-VImTFSI)-MWNTs at 60C and coulombic efficiency.*



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