

PEDOT Radical Polymer with Synergetic Redox and Electrical Properties

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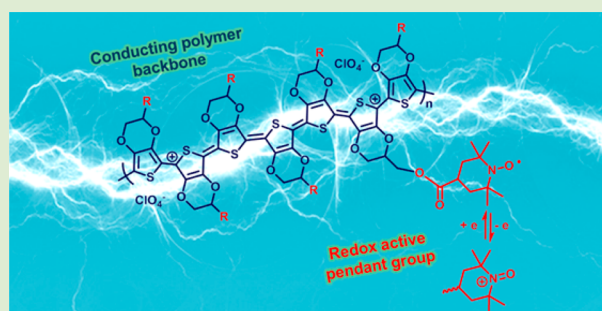
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S Supporting Information

ABSTRACT: The development of new redox polymers is being boosted by the increasing interest in the area of energy and health. The development of new polymers is needed to further advance new applications or improve the performance of actual devices such as batteries, supercapacitors, or drug delivery systems. Here we show the synthesis and characterization of a new polymer which combines the present most successful conjugated polymer backbone and the most successful redox active side group, i.e., poly(3,4-ethylenedioxythiophene) (PEDOT), and a nitroxide stable radical. First, a derivative of the 3,4-ethylenedioxythiophene (EDOT) molecule with side nitroxide stable radical group (TEMPO) was synthesized. The electrochemical polymerization of the PEDOT-TEMPO monomer was investigated in detail using cyclic voltammetry, potential step, and constant current methods. Monomer and polymer were characterized by NMR, FTIR, matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS), electron spin resonance (ESR) spectroscopy, elemental analysis, cyclic voltammetry, and four-point probe conductivity. The new PEDOT-TEMPO radical polymer combines the electronic conductivity of the conjugated polythiophene backbone and redox properties of the nitroxide group. As an example of application, this redox active polymer was used as a conductive binder in lithium ion batteries. Good cycling stability with high Coulombic efficiency and increased cyclability at different rates were obtained using this polymer as a replacement of two ingredients: conductive carbon additive and polymeric binders.



Redox active polymers have been of increasing interest due to the capability to change their chemical, electronic, optical, or mechanical properties depending on the redox state.¹ The reversibility of the redox process makes these polymers target materials for different applications such as batteries, biosensors, electrochromic devices, organic solar cells, bio-actuators, and nanomedicine.^{2–7} Polymers with redox properties are those with the ability of changing their electrochemical properties with the oxidation state due to the loss of electrons (oxidation) or the gain of electrons (reduction). The IUPAC definition for a redox polymer is a polymer-containing group that can be reversibly reduced or oxidized. Reversible redox reactions can take place in the polymer main chain, as in the case of conducting polymers such as polyaniline,⁸ or in side groups, as in the case of a polymer carrying ferrocene side groups. Here we show the synthesis and characterization of a new polymer which combines both the most successful redox active conjugated polymer backbone and the most successful side group.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is nowadays the commercially available and widely used conducting polymer

having a redox-active conjugated backbone.⁹ PEDOT can be synthesized by electrochemical polymerization¹⁰ or by oxidative chemical polymerization to obtain aqueous dispersions stabilized by a water-soluble poly(styrenesulfonate). PEDOT presents high electrical conductivity (up to 10³ S/cm), good transparency, and excellent electrochemical and thermal stability.^{11–14} As one of the applications, PEDOT and other conducting polymers have been used as cathode and anode materials in batteries.^{15–17} However, they possess relatively low specific energy density, and several recent works have reported the attachment of redox moieties such as anthraquinones to increase its performance.¹⁸

Polymers containing stable organic radical moieties as pendant groups or radical polymers are attracting much attention for their high charge transfer reactions and the possibility to create p-type and n-type radical polymers

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Scheme 1. Synthesis of EDOT-TEMPO Monomer and Its Electrochemical Polymerization

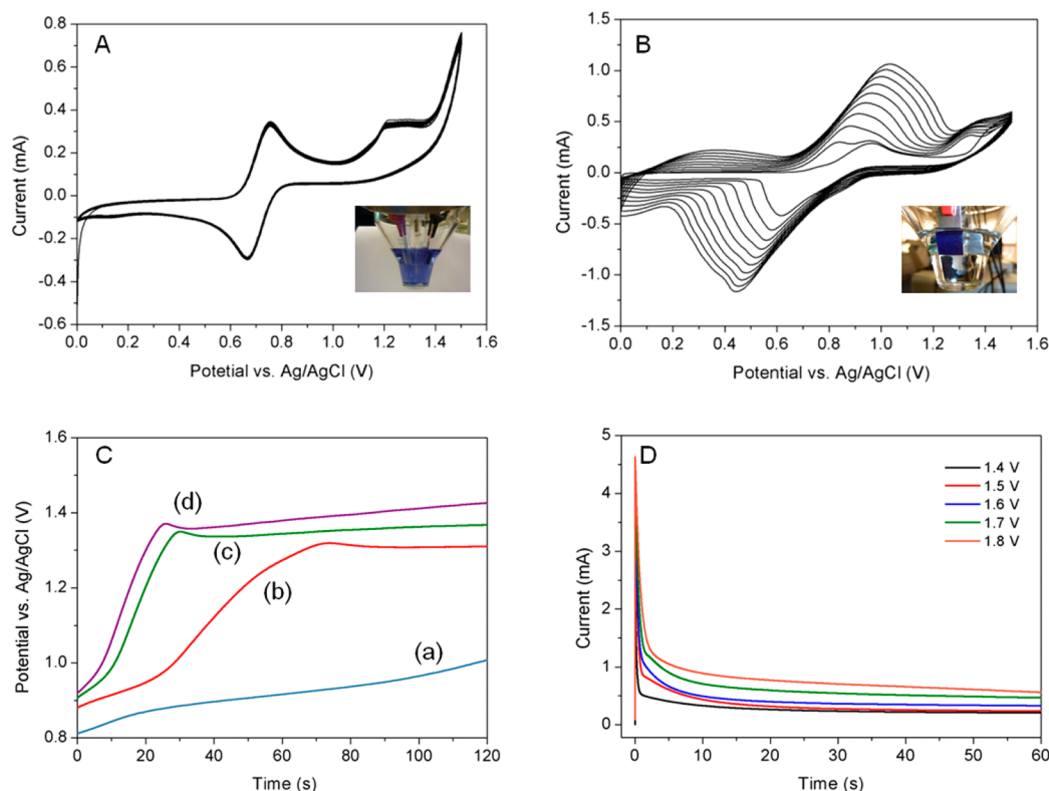
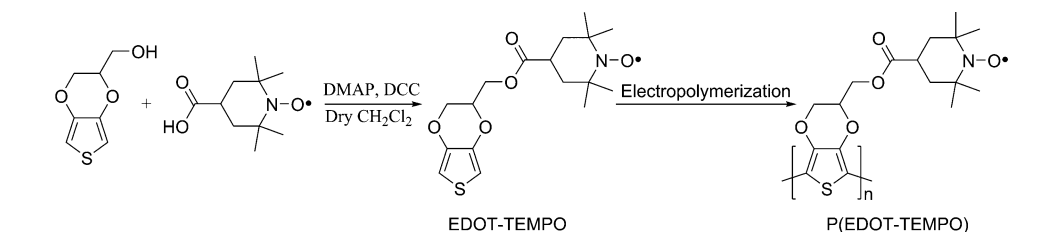


Figure 1. Cyclic voltammograms of the electrochemical polymerization in 10^{-3} M EDOT-TEMPO and 0.1 M LiClO_4 acetonitrile solution (A) and in 0.1 M TBAPF_6 dichloromethane solution (B), using a 1 cm^2 electrode, switching potential from 0.0 to 1.5 V at a 20 mV s^{-1} scan rate. Insets show the pictures of the cell after the electropolymerization. (C) Chronopotentiograms obtained from a 10^{-3} M EDOT-TEMPO and 0.1 M TBAPF_6 dichloromethane solution at constant currents of (a) 0.10, (b) 0.15, (c) 0.20, and (d) 0.25 mA and (D) chronoamperograms obtained from the same monomeric solution at potential steps between 1.4 and 1.8 V, using a 1 cm^2 electrode.

depending on the functional pendant group.^{19–21} Nishide and co-workers first developed polymers containing stable nitroxide radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).²² Batteries with these organic radical polymers have good cycling stability, fast charge–discharge rates, and high power density.^{23,24} Most of the radical polymers have nonconjugated macromolecular backbones. Actual trends include the attachment of different types of stable radicals, development of new macromolecular architectures such as block copolymers or the further physicochemical understanding, and new applications of these polymers in optoelectronics. It is worth mentioning that Aydin et al. have recently reported the synthesis of a polymer having a semiconjugated backbone and a nitroxide pendant group which shows a limited performance in a battery probably due to the low stability of the chosen polymer backbone.²⁵

In this study, we present the synthesis and characterization of a new polymer which combines both a poly(3,4-ethylenedioxythiophene) (PEDOT) backbone and a nitroxide stable

radical (TEMPO) side chain. For that purpose, the synthesis of the 3,4-ethylenedioxythiophene derivative monomer bearing a TEMPO nitroxide radical was carried out. Its electrochemical polymerization and the characterization of the obtained redox active and electrically conductive PEDOT-TEMPO polymer were investigated. The PEDOT-TEMPO polymer shows a unique combination of redox and electrical properties. As a potential application the results of the use of the polymer as a conductive binder in LiFePO_4 batteries are presented.

The new EDOT-bearing TEMPO monomer was synthesized via esterification reaction between EDOT-MeOH and 4-carboxy-TEMPO in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) in dry dichloromethane with a high yield (Scheme 1). The esterification reaction was proven by ATR-FTIR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. ATR-FTIR spectroscopy (Figure S1A, Supporting Information) shows absorption at 1724 cm^{-1} due to the presence of the carbonyl stretching which is higher than the reactant carboxylic acid

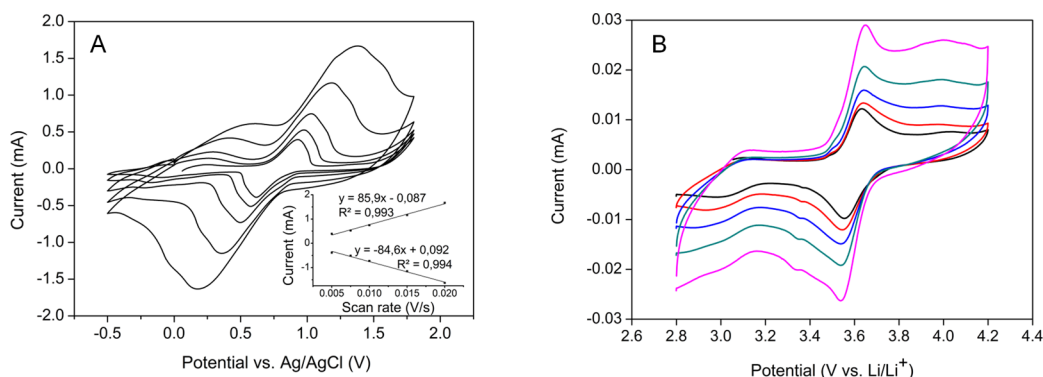


Figure 2. (A) Cyclic voltammograms of PEDOT-TEMPO film in 0.1 M TBAPF₆ dichloromethane solution at 5, 7.5, 10, 15, and 20 mV s⁻¹. Inset graph shows the relationship between the oxidation and reduction peak currents vs scan rate. (B) Cyclic voltammograms of PEDOT-TEMPO/C (70/30) electrode with 1 M LiPF₆ in EC:DMC electrolyte at 0.05, 0.1, 0.2, 0.4, and 0.8 mV s⁻¹.

(1685 cm⁻¹) and a lack of O–H stretching band at around 3200 cm⁻¹. The monomer was characterized by MALDI-TOF mass spectrometry using a positive-ion reflectron mode. Figure S2 shows an enlargement of the obtained MALDI spectral peaks for the monomer and the comparison with theoretical isotopic distribution. The electron spin resonance (ESR) spectrum of the monomer in toluene solution shows a triplet with nitrogen hyperfine splitting constant of 14.4 G (Figure S3) which is characteristic of TEMPO nitroxide radicals.

Then, the electrochemical polymerization of the EDOT-TEMPO monomer was investigated by cyclic voltammetry in acetonitrile and dichloromethane at a 20 mV s⁻¹ scan rate, switching the potential between 0.0 and 1.5 V. When the electrochemical polymerization was carried out in acetonitrile (Figure 1A), the nitroxide group was oxidized at 0.75 V and reduced at 0.65 V, while the thiophene ring was oxidized at potentials higher than 1.40 V, leading to the polymerization. During the polymerization, the material that was formed on the electrode was simultaneously dissolved in the electrolyte leading to a blue-colored solution, as shown in the inset of Figure 1A.

When the electropolymerization was carried out in dichloromethane solution (Figure 1B), the polymerization started at 1.35 V with the oxidation of EDOT, while the TEMPO group of the monomer was oxidized and reduced at 0.95 and 0.62 V, respectively. When increasing the number of cycles, the current and the potential of the maxima increased showing the growing amount of polymer electrodeposited onto the electrode during every sweep. The potential of the oxidation peak maxima varies from the first to the second cycle, in the case of EDOT from 1.42 to 1.34 V and from 0.95 to 0.82 V for TEMPO. This behavior is usual in conducting polymers since the oxidation on the coated polymer electrode needs lower potential than the oxidation on the platinum electrode.

Due to the electrochromic characteristics of PEDOT polymers that are colorless in their oxidized state and colored in their reduced state, it was not possible to observe the formation and growth of the film during the anodic electropolymerization; only during reduction the blue film was observed. The color change from colorless to blue was observed at potentials lower than 0.2 V.

The electropolymerization was also investigated by applying constant current flows of 0.10, 0.15, 0.20, and 0.25 mA through previously cleaned platinum electrodes for 60 s (Figure 1C). When 0.10 mA constant current was applied, 60 s was not sufficient for the electropolymerization since the potential

reached was lower than the onset of the monomer oxidation. For higher currents, the electropolymerization occurred at almost constant potential between 1.3 and 1.4 V, which is the oxidation potential of the monomer, and the voltage plateau was higher when the applied current was increased.

The electropolymerization was also carried out by potential steps from 0 V to different potentials ranging between 1.4 and 1.8 V, which are higher than the onset of the monomer oxidation (Figure 1D). In the chronoamperograms obtained at the potential steps of 1.4 and 1.5 V, after an initial current leap a minimum and a shoulder are present which are representative of a nucleation process of PEDOT-TEMPO on the platinum electrode. When higher potentials are applied, a high initial peak is followed by a fast current decrease. The stationary current obtained after the initial peak is higher when applying a higher anodic potential. The electrochemical characterization of the formed films showed a similar voltammogram to the one obtained by electropolymerization by cyclic voltammetry, indicating that the electropolymerization occurs via the same mechanism.

The electrodeposited PEDOT-TEMPO film in dichloromethane was later electrochemically characterized in a monomer-free 0.1 M TBAPF₆ dichloromethane solution. The cyclic voltammograms of the polymer obtained when sweeping the potential between -0.5 and 1.8 V at different scan rates are shown in Figure 2A. The polymer shows two redox processes: the first one related to the PEDOT backbone which is oxidized at 0.3 V and reduced at around -0.2 V and the second one to the TEMPO group that is oxidized and reduced at 0.92 and 0.6 V, respectively, at a 5 mV s⁻¹ scan rate. The cathodic and anodic peak currents of TEMPO show a linear dependence on the scan rate indicating that the redox processes are not diffusion limited (inset of Figure 2A). The electrochemical behavior of a cathode consisting of 70% of PEDOT-TEMPO electropolymerized in acetonitrile and 30% of carbon was investigated versus a lithium anode by sweeping the potential between 2.8 and 4.2 V at different scan rates (Figure 2B). In the same manner of the film, the PEDOT-TEMPO cathode shows two main redox processes. The TEMPO group shows its oxidation and reduction at 3.65 and 3.55 V, respectively, while the PEDOT backbone redox activity is observed around 3.0 V.

The nature of the PEDOT backbone was confirmed by FTIR and UV spectroscopies shown in Figure S1. The typical bands associated with thiophene ring vibrations were identified in the FTIR spectrum of the polymer (1517, 1355, 1304 cm⁻¹) as well as the carbonyl (1727 cm⁻¹) and nitroxide (1362 cm⁻¹) bands.

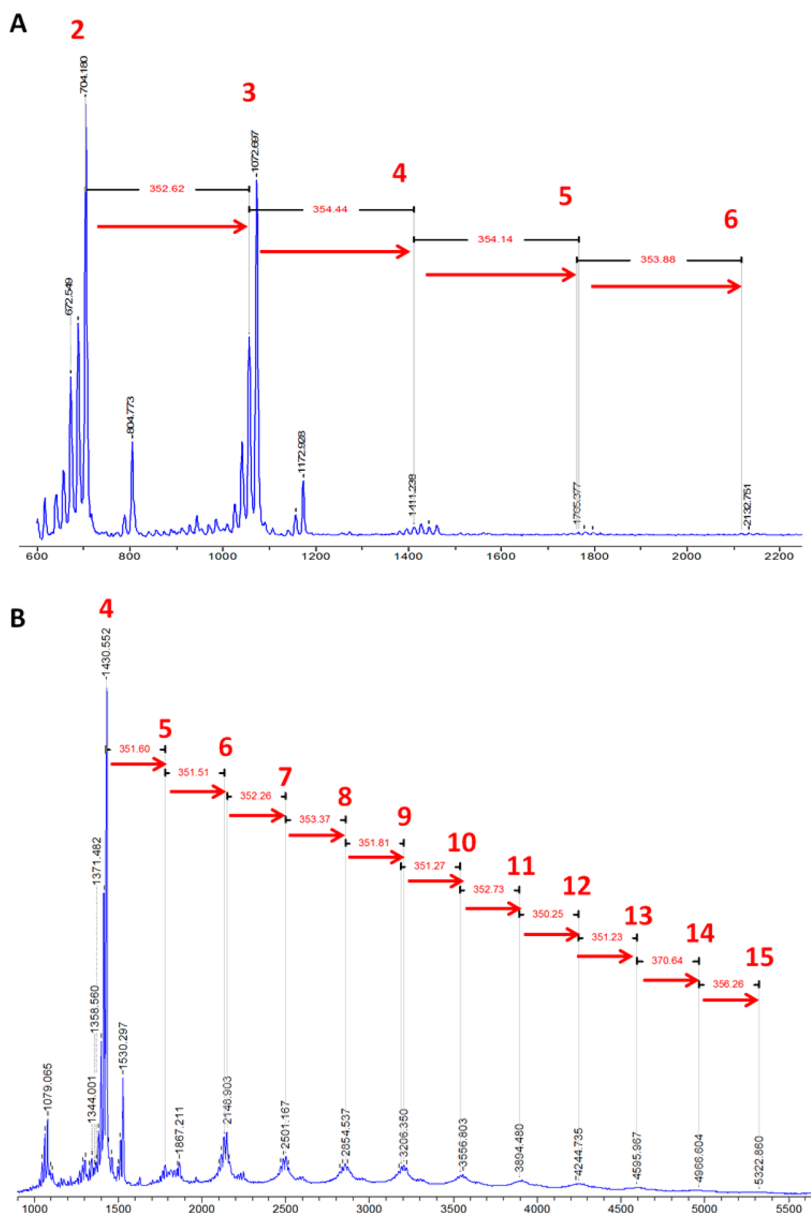


Figure 3. MALDI-TOF mass spectra of PEDOT-TEMPO in the positive ion linear mode in different mass ranges (A) 600–2200 Da (deflection below 600 Da) and (B) 1000–5500 Da (deflection below 1000 Da).

The UV–vis spectrum of the EDOT-TEMPO monomer shows absorption at 239 and 256 nm. The latter peak related to the EDOT group shifts to higher wavelengths during the polymerization, as the π system conjugation becomes longer. The UV–vis spectrum of the polymer soluble in acetonitrile shows absorption at 312 nm related to oligomeric units, absorption at 567 and 609 nm corresponding to π – π^* transitions in PEDOT backbone, and the typical polaronic–bipolaronic bands with maximum absorption at 776 and 875 nm.

Interestingly, MALDI-TOF mass spectrometry was used to analyze the molar mass distributions of the electropolymerized PEDOT-TEMPO. Using the positive ion linear mode, the molar mass distribution (MMD) and the number of monomeric units were determined. The obtained MMD values for PEDOT-TEMPO are $M_n = 1759$, $M_w = 2033$, and polydispersity (\bar{D}) of 1.16. The correct repeating unit of 352 Da is observed between the peaks of different series, and

oligomers up to 15 monomeric units are detected. Figure 3 shows the spectra of PEDOT-TEMPO in two different mass ranges. In order to avoid the ion suppression effect at low molecular weight (LMW) and achieve detecting peaks in high molecular weight (HMW), it was necessary to do deflection of the sample below 600 and 1000 Da. The red arrows show the increment of a monomer in the oligomer. The number above the peaks denotes the total number of monomer units in the oligomer.

Furthermore, the presence of the radical nitroxide in the obtained PEDOT-TEMPO polymer was investigated by ESR. The ESR spectrum of the polymer was recorded in acetone solution (Figure S3). The polymer shows a triplet similar to the monomer spectrum, with the usual hyperfine coupling constant of 14.4 G, which indicates that the polymer is bearing nitroxide radicals. As the measurement was done in acetone solution, the spectrum shows signals of Mn^{2+} ion hyperfine structure coming from the capillary.

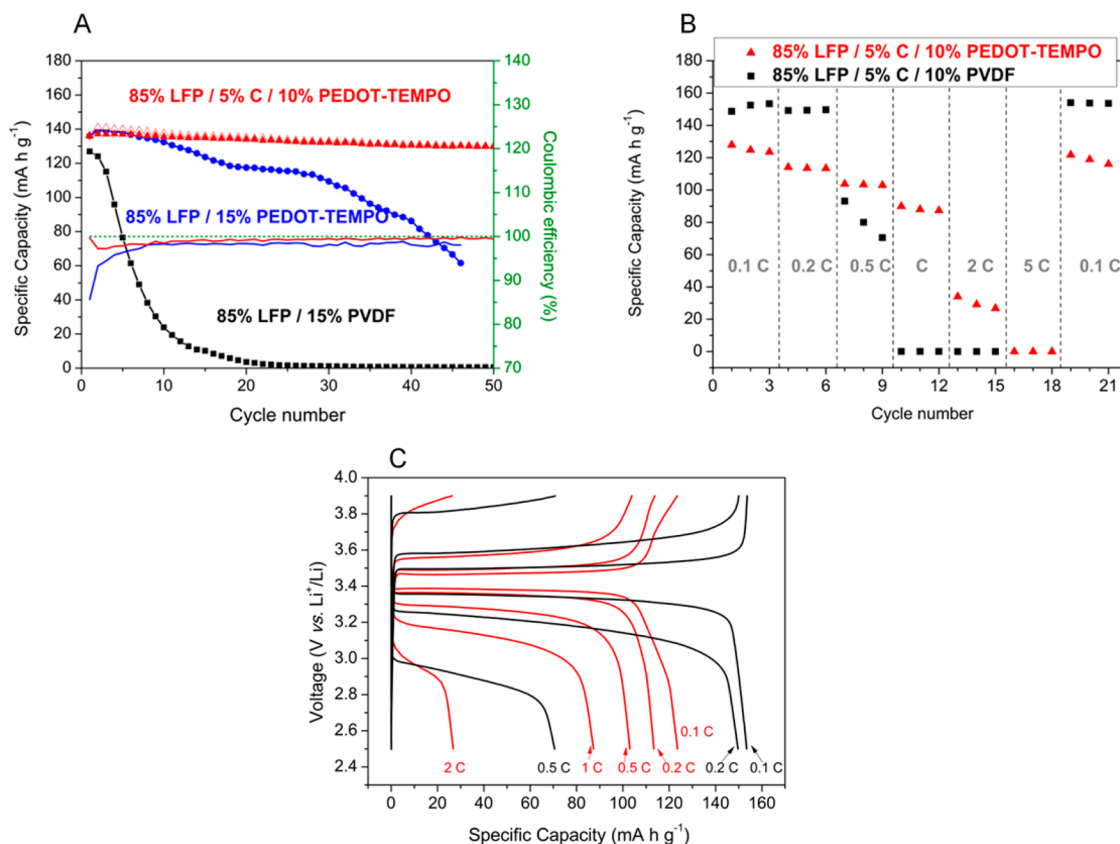


Figure 4. Cell performance of LFP cathodes. (A) Discharge capacity and Coulombic efficiency at 0.1 C with (blue circle) 15% PEDOT-TEMPO, (red triangle) 10% PEDOT-TEMPO and 5% carbon, and (black square) 15% PVDF. (B) C-rate capability and (C) voltage profile at different C rates for (red line) 10% PEDOT-TEMPO and 5% carbon and (black line) 10% PVDF and 5% carbon.

The electrical conductivity of electropolymerized PEDOT-TEMPO was measured by the four-point probe technique. For the measurements, the obtained polymer in acetonitrile was drop casted on glass slides to obtain films of around 10 μm thickness. The average conductivity value of three films was 5.7×10^{-2} S/cm. This value is relatively low when compared to PEDOT conductivity (1×10^3 S/cm) but similar to the electrical conductivity reported for other PEDOT derivatives based on substituted EDOT monomers.²⁶ On the other hand, this value compares very favorably with the conductivity of conventional radical polymers which show conductivity values between 10^{-5} and 10^{-7} S/cm.¹⁹

The redox nature and activity of the polymer were confirmed by ESR and electrochemical characterization, while the chemical structure and electrical properties were studied by FTIR, UV-vis, MALDI-TOF MS, and four-point probe. Altogether, the different characterizations carried out confirmed the synthesis of a PEDOT radical polymer with synergetic redox and electrical properties.

As a potential application, the redox-active conductive PEDOT-TEMPO was used as a conductive binder in lithium-ion batteries. Conventional lithium-ion cathodes are usually made of three main components: an active material (LiFePO₄, LiCoO₂ etc.), a conductive additive such as carbon, and a polymeric binder. Conductive polymers have been mostly applied as conductive coatings of current Li-ion insulating inorganic cathode materials such as LiCoO₂ or LiFePO₄.^{27–29} On the other hand, Gohy and collaborators have recently shown that the presence of radical polymers allowed us to increase the electron transfer kinetics of LiFePO₄ electrodes

and cycling ability of the batteries at high C rates.^{30,31} Furthermore, in order to obtain high energy density batteries, the use of conductive additives and binders that are not redox active should be decreased to have the maximum active material into a fixed volume of electrode. So in principle our PEDOT-TEMPO polymer may be ideally suited to be used as conducting binder due to its synergetic properties.

The performance of PEDOT-TEMPO as a conductive binder was investigated in LiFePO₄ (LFP) cathodes and compared to its counterpart cathode containing a conventional binder, poly(vinylidene fluoride) (PVDF). The cell performance of the cathode without carbon added consisting of 85% LFP and 15% PEDOT-TEMPO is shown in Figure 4A. The charge/discharge capacity of the cell containing PEDOT-TEMPO is higher than the counterpart having PVDF as binder, whose capacity decreases drastically in the first cycles due to a lack of electron transport between cathode components. This confirms that PEDOT-TEMPO can act as a conductive binder, providing high Coulombic efficiency (98%); however, the discharge capacity is not completely stable. After addition of a minimum amount of carbon, the stable discharge capacity of the PEDOT-TEMPO cell was obtained (95% capacity retention after 50 cycles) together with high Coulombic efficiency (>99%) at the 0.1 C rate.

The rate capability of the cells with the latter configuration was also investigated (Figure 4B). Although a cathode with PVDF binder provides higher capacity deliverance at low C rates (0.1 and 0.2 C), higher C rate performance (0.5, 1, and 2 C) was dominated by a cathode with PEDOT-TEMPO binder with a capacity of 90 mA h g⁻¹ at 1 C rate. The voltage profiles

at different rates are shown in Figure 4C where the polarization of the cathode containing PVDF binder at C rates higher than 0.2 C is noticeable.

In conclusion, the synthesis of a novel EDOT derivative bearing a TEMPO nitroxide radical has been presented in this work. The monomer has been polymerized by electrochemical techniques, and the obtained polymer presents combined properties of both groups, electronic conductivity of the PEDOT backbone together with the redox activity of the TEMPO moiety. Interestingly, the electropolymerization in acetonitrile led to a soluble polymer. These properties make PEDOT-TEMPO a good candidate to be used as a conductive binder in batteries. Its performance as a binder was investigated in LiFePO₄ batteries and compared to the conventional PVDF binder. Good cycling stability with high Coulombic efficiency and increased C rate capability were obtained with 85% LFP/5% C/10% PEDOT-TEMPO cathode configuration. Therefore, PEDOT-TEMPO can act as a conductive binder, thus replacing the conventional binder and reducing the amount of high surface area carbon additive generally required to improve electrical conductivity in insulating cathode materials.

■ ASSOCIATED CONTENT

● Supporting Information

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Experimental details and additional supporting figures (PDF)

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Notes

The authors declare no competing financial interest.

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