Polymer xxx (2015) 1–7

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis, characterization and charge–discharge studies of ferrocene-containing poly(fluorenylethynylene) derivatives as organic cathode materials

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ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form
20 January 2015
Accepted 22 January 2015
Available online xxx

Keywords:
Ferrocene
Poly(fluorenylethynylene)s
Organic cathode materials

ABSTRACT

Two new poly(fluorenylethynylene)s with ferrocene moieties **PFFAL1** and **PFFAL2** were designed and synthesized. Their structures, molar masses, photophysical properties and thermal characteristics were analyzed by ^{1}H NMR, Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC), ultraviolet–visible (UV–Vis) spectroscopy and thermogravimetric analysis (TGA). The morphologies and electrochemical performances of the polymer-composed cathodes were studied by scanning electron microscopy (SEM), cyclic voltammetry (CV) and galvanostatic charge–discharge test. The results showed that **PFFAL1**-composed electrode retained over 90% of the initial capacity after 100 cycles at 10 C and **PFFAL2**-based cathode exhibited a stable discharge capacity of 73 mAh g^{-1} at 1 C, which is close to the theoretical value (82.3 mAh g^{-1}). The stable capacity as well as the good cycle endurance of these polymer-based coin cells revealed their great potential as cathode-active materials for rechargeable lithium batteries.

1. Introduction

The ever growing energy demands and global environmental issues are recognized as two major challenges in today's modern society. To tackle these problems, two promising sustainable energy sources, solar power and wind, will play an increasingly important role in the coming years [1]. While there is a widespread utilization of solar and wind energy, new problems associated with electrochemical energy storage (EES) will be brought out by the increase of our dependence on these interruptible natural resources [2]. Meanwhile, continuous progress in portable electronic applications, such as touch screens and rollup displays, also places a huge burden on the implementation of efficient energy-storing devices [3].

Among various electrical storage technologies, rechargeable lithium-ion batteries are undoubtedly one of the most simple and reliable devices, which facilitate the conversion between electrical power and chemical energy by reversible electrochemical redox reactions [4,5]. However, in the research of efficient and portable rechargeable lithium-ion batteries, development of good cathode material is always the bottleneck issue [6]. The ideal features of organic redox-active molecules, such as structure diversity, device flexibility, environmental friendliness and solution processability, make them a promising candidate for next-generation batteries [7,8]. Extensive efforts have recently been dedicated to develop sustainable organic cathode materials including conducting polymers [9–13], organosulfur molecules [14–23], organic radical polymers [24–29], carbonyl compounds [30–38] and some other organic structures [39–45].

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http://dx.doi.org/10.1016/j.polymer.2015.01.054
0032-3861/

Ferrocene ($Fe(C_5H_5)_2$, C_5H_5 = cyclopentadienyl) is a famous organometallic compound with a unique sandwich-like structure that could be oxidized to ferrocenium cation ($Fe(C_5H_5)_2^+$). This oxidation reaction was proved to be reversible, and the one-electron exchange rate constant for $Fe(C_5H_5)_2^+/Fe(C_5H_5)_2$ redox system could reach up to 7×10^{-1} cm s^{-1} [46]. Combined with other distinguished features such as excellent stability and solvent-independent redox property, ferrocene is therefore turned into the most well-known standard reference applied in cyclic voltammetry measurements [47]. In recent years, several attempts on ferrocene-based organic molecules for active cathode materials have been reported. However, most known systems suffer from low molar masses and therefore unstable electrodes [48–52]. In search of efficient organic cathode materials, poly(fluorenylethynylene) derivatives with a high degree of polymerization are large organic molecules which will not dissolve in commonly used electrolytes, and thus provide a direct and valid way to get stable electrodes. Meanwhile, owing to the overlapping π-orbitals of alternating double- and single-bonds, π-electrons in conjugated polymers can be easily moved from one bond to the other, which is also beneficial to the desired fast kinetics for electrode materials [53]. Herein, two new conjugated poly(fluorenylethynylene) type polymers bearing ferrocene moieties **PFFAL1** and **PFFAL2** were designed and synthesized. Their structural determinations, optical properties, thermal characteristics and redox behaviors were systematically investigated. Moreover, after the fabrication of a composite electrode consisting of the synthesized polymers, vapor-grown carbon nanofibers (VGCF) and poly(vinylidenefluoride) (PVDF), their charge–discharge performances as cathode active materials for rechargeable lithium batteries were studied.

2. Experimental section

2.1. Materials

All the reactions were carried out under a nitrogen atmosphere. All materials for the chemical synthesis were purchased from Sigma–Aldrich, J&K or Acros Organics and used without further purification. Commercially available reagents were used as received unless otherwise noted. The solvents used in the polymerization reactions were dried and distilled appropriately prior to use. **FFA** [54,55] and **L2** [56] were synthesized according to the methods as described in the literature.

2.2. General procedures

^1H NMR and ^{13}C NMR spectra were measured in deuterated solvents on a Bruker AV 400 MHz FT-NMR spectrometer, where chemical shifts (δ in ppm) were quoted with tetramethylsilane as the internal standard for ^1H and ^{13}C nuclei. Size exclusion chromatography (SEC) was analyzed by using Agilent 1050 HPLC system with visible wavelength and fluorescent detector. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 1000 PC spectrometer. UV-Vis absorption spectra were obtained on a HP-8453 diode array spectrophotometer. TGA measurements were performed with a Perkin–Elmer TGA6 thermal analyzer.

2.3. Electrochemical analysis

A three electrode set-up was used (WE: glassy carbon disk, RE: $AgNO_3/Ag$ in THF 0.1 M n-Bu_4NPF_6, CE: Pt wire) for cyclic voltammetry. The redox couple of ferrocenium/ferrocene (Fc^+/Fc) was utilized as the internal standard. All electrolytes were degassed with dry argon and all measurements were performed under an argon atmosphere. Electrodes were prepared by adding a solution of the polymer and PVDF (Sigma–Aldrich) in NMP (10 mg/mL) to VGCF (Sigma–Aldrich) as conducting additives (polymer/VGCF/PVDF, 10/80/10, *w*/*w*/*w*). These materials were mixed in a montar for 10 min and more NMP was added to give a paste. The thus-obtained paste was coated on a graphite foil (Alfa Aesar) by applying the doctor blading method. Next, NMP was removed by heating the electrodes at 40 °C under high vacuum for 24 h.

2.4. Preparation of coin cells

A solution of the polymer and PVDF in NMP (10 mg/mL) was added to VGCF as conducting additive (polymer/VGCF/PVDF, 10/80/10, *w*/*w*/*w*). More NMP was added and the materials were mixed in a mortar for 10 min. The paste was coated on an aluminum foil (thickness: 0.015 mm, MTI Corporation) by applying the doctor blading method. Next, the NMP was removed at 40 °C under high vacuum for 24 h. After drying, the amount of active material on the electrode was determined on the basis of the weight of the electrodes. The coin cells (type 2032) were manufactured under an argon atmosphere. Suitable, round composite electrodes (15 mm diameter) were cut with a MTI Corporation Precision Disc Cutter T-0.6. This electrode employed as cathode was placed into the bottom cell case and separated from the lithium anode by a porous polypropylene membrane (celgard, MTI Corporation). On top of the lithium anode (lithium foil, Sigma–Aldrich), a stainless steal space (diameter: 15.5 mm, thickness: 0.3 mm, MTI Corporation) and a stainless steal wave spring (diameter: 14.5 mm, height 1.2 mm) were placed. The cell was filled with electrolyte (propylene carbonate, 0.5 M lithium perchlorate) and the top cell case was placed onto the electrode. The cell was sealed with an electric crimper machine (MTI Corporation MSK-100D). Electrochemical measurements were performed after an equilibration time of 24 h. All experiments were performed at room temperature.

2.5. Synthesis of **PFFAL1**

To a mixture of **FFA** (56 mg, 0.136 mmol) and **L1** (46 mg, 0.136 mmol) in a mixed solution of triethylamine (10 mL) and dry THF (10 mL) under nitrogen were added copper iodide (2 mg, 0.0068 mmol) and tetrakis(triphenylphosphine)palladium (8 mg, 0.0068 mmol). The solution was stirred for 30 min at room temperature and was then heated to reflux overnight. After completion of the reaction, the solvent was removed under reduced pressure. The residue was chromatographed over a silica gel column by eluting with dichloromethane and tetrahydrofuran to give a red solid, which was precipitated in hexane to afford the desired compound. Anal. Calc. for $C_{32}H_{18}SFe$: C, 78.37; H, 3.70. Found: C, 78.65; H, 3.88. ^1H NMR (tetrahydrofuran-d_8, 400 MHz): δ 8.48 ~ 8.45 (m, 1H, fluorenyl H), 8.19 ~ 8.12 (m, 1H, fluorenyl H), 7.90 ~ 7.76 (m, 3H, fluorenyl H), 7.57 ~ 7.56 (m, 2H, fluorenyl H and vinyl H), 7.49 ~ 7.32 (m, 1H, thiophenyl H), 7.29 ~ 7.24 (m, 1H, thiophenyl H), 4.85 (br, 2H, Fc), 4.64 (br, 2H, Fc), 4.31 ~ 4.30 (m, 5H, Fc). IR (KBr pellet, cm^{-1}): 3086 (C–H stretching, Fc), 2190 (C≡C stretching), 1622 (C═C stretching, Ar), 1596 (C═C stretching, Ar), 1456 (C═C stretching, Ar), 1411 (C═C stretching, Fc), 1103 (C–C stretching, Fc), 1000 (C–C stretching, Fc), 815 (C–H bending, Fc), 488 (C-Fc).

2.6. Synthesis of **PFFAL2**

PFFAL2 was synthesized similar to **PFFAL1** except that **L2** (68 mg, 0.136 mmol) was used instead of **L1**. Anal. Calc. for $C_{46}H_{28}NFe$: C, 84.92; H, 4.34; N, 2.15. Found: C, 85.10; H, 4.56; N, 2.24. ^1H NMR (tetrahydrofuran-d_8, 400 MHz): δ 8.47 ~ 8.45 (m, 1H, fluorenyl H), 8.20 ~ 8.07 (m, 1H), 7.86 ~ 7.76 (m, 4H), 7.62 ~ 7.56 (m, 2H, Ar and vinyl CH), 7.53 ~ 7.47 (m, 2H), 7,46 ~ 7.38 (m, 2H),

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7.35 ~ 7.27 (m, 2H), 7.18 ~ 7.01 (m, 5H), 6.92 ~ 6.88 (m, 1H), 4.83 (br, 2H, Fc), 4.63 ~ 4.59 (m, 2H, Fc), 4.31 ~ 4.28 (m, 5H, Fc). IR (KBr pellet, cm^{-1}): 3032 (C—H stretching, Fc), 2197 (C≡C stretching), 1624 (C═C stretching, Ar), 1588 (C═C stretching, Ar), 1503 (C═C stretching, Ar), 1484 (C═C stretching, Ar), 1413 (C═C stretching, Fc), 1106 (C—C stretching, Fc), 1001 (C—C stretching, Fc), 817 (C—H bending, Fc), 500 (C—Fe).

3. Results and discussion

3.1. Synthesis and characterization

Two comonomers were utilized for polymerization to enable on one hand the straightforward synthesis of a polymer with only one redox center (2,5-diiodothiophene **L1**) and on the other hand an advanced system with higher capacity (4,4′-diiodotriphenylamine **L2**). **L2** was synthesized through direct iodination of triphenylamine under an acidic condition by carefully controlling the equivalent amounts of KIO_3 and KI as well as the reaction time [56].

In the presence of triethylamine, tetrakis(triphenylphosphine) palladium and copper(I) iodide, polymers **PFFAL1** and **PFFAL2** were synthesized *via* a Sonogashira cross-coupling polycondensation of ferrocene-based fluorene derivative **FFA** and diiodo-substituted monomers **L1** and **L2**, respectively (Scheme 1).

As the conjugated polymers **PFFAL1** and **PFFAL2** are almost insoluble in commonly used chlorinated organic solvents, deuterated tetrahydrofuran (THF-d_8) was employed for NMR analysis (SI, Figs. S1—S3). All signals in the ^{1}H NMR spectra are consistent with their structures. Protons at $\delta = 4.20$ ~ 4.87 ppm are assigned to the ferrocene unit, while peaks at $\delta = 6.50$ ~ 8.80 ppm are attributed to the aromatic rings and the vinyl protons. The near completeness of the polymerizaion could be confirmed because of the disappearance of the terminal acetylenic protons at $\delta = 3.53$ and 3.61 ppm in **FFA**. Compared with the corresponding signals in monomers, all protons in polymers are downfield shifted, which is possibly caused by the increased deshieding effect of the enlarged conjugated systems. Meanwhile, the peaks of the polymers shown in the ^{1}H NMR spectra are broadened as expected.

The comparative FTIR spectra of the synthetic poly(fluorenylethynylene)s and the corresponding monomer **FFA** were analyzed (Fig. 1). As for **PFFAL1**, the alkyne C≡C vibration is shifted from 2099 cm^{-1} to 2191 cm^{-1}, and the peaks at 3086, 1411, 1103, 1000, 815 and 488 cm^{-1} are the characteristic signals of ferrocene. The alkyne C≡C vibration signal of **PFFAL2** is also shifted to 2197 cm^{-1}. The transmission peaks at 3032, 1413, 1106, 1001, 817 and 500 cm^{-1} are ascribed to ferrocene. These FTIR results could further confirm the completeness of the coupling polymerization.

The molar masses of **PFFAL1** and **PFFAL2** were estimated *via* SEC (Table 1). Notably, **PFFAL1** with the thiophene moiety gets the highest molar mass and the largest polydispersity index among the obtained polymers.

3.2. Photophysical properties

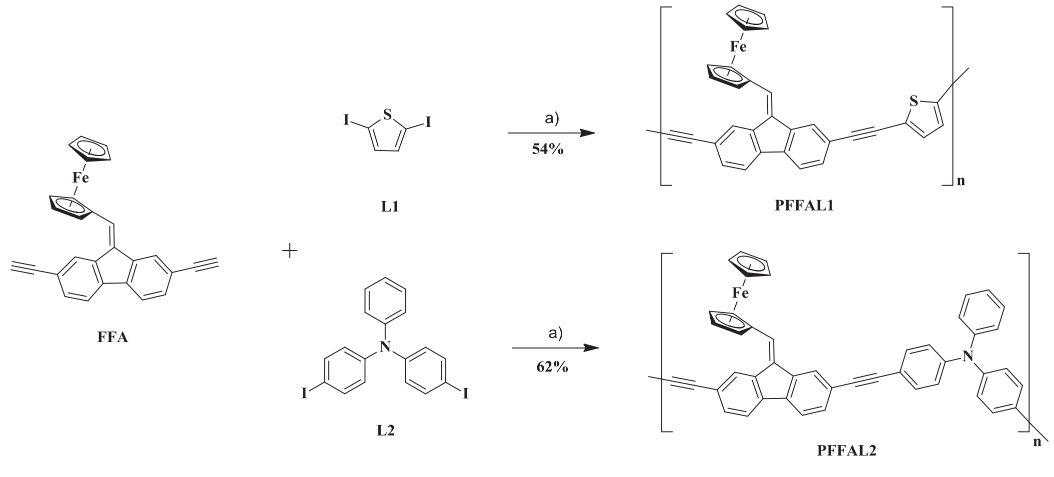
The optical features of **PFFAL1** and **PFFAL2** were investigated by UV—Vis spectroscopy (Fig. 2). It can be seen that **PFFAL1** shows five absorption peaks at 239, 265, 288, 389 and 512 nm. In comparison with the related monomers, the absorption signals at 239 and 288 nm are likely to result from the electronic transitions of the thiophene moiety, and the peaks at 265, 389 and 512 nm possibly correspond to the fluorene unit of **PFFAL1**. The conjugated polymer **PFFAL2** exhibits five absorption peaks at 239, 267, 292, 381 and 505 nm. The absorptions at 239 and 292 nm correspond to the electron transitions of the triphenylamine moiety, while the signals at 267, 381 and 505 nm are assigned to the ferrocene unit. These results indicate that **PFFAL2** contains both ferrocene and triphenylamine moieties. The absorption peaks of all conjugated polymers are obviously red-shifted, which is attributed to the extension of the π-conjugated systems after the polymerization. As a result, the transport of the active charged species along the main chain of the conjugated polymers is improved, which is very important for high-performance rechargeable lithium-ion batteries [51].

3.3. Thermal characteristics

As a high thermal stability is crucial for lithium-ion batteries from the viewpoint of safety, the thermogravimetric analyses of the ferrocene-containing conjugated polymers **PFFAL1** and **PFFAL2** were performed (SI, Fig. S4), and the results show that these prepared polymers are thermally stable up to 350 °C without decomposition.

3.4. Electrochemical performances

The electrochemical stability of the two ferrocene-containing polymers was studied initially in solution. Fig. 3 displays the cyclic voltammograms of **PFFAL1** and **PFFAL2** in THF solution. The cyclic voltammogram of **PFFAL1** exhibits only the oxidation of



a) CuI, $Pd(PPh_3)_4$, Et_3N, dry THF, 70 °C, 24 h

Scheme 1. Schematic representation of the synthesis of **PFFAL1** and **PFFAL2**.

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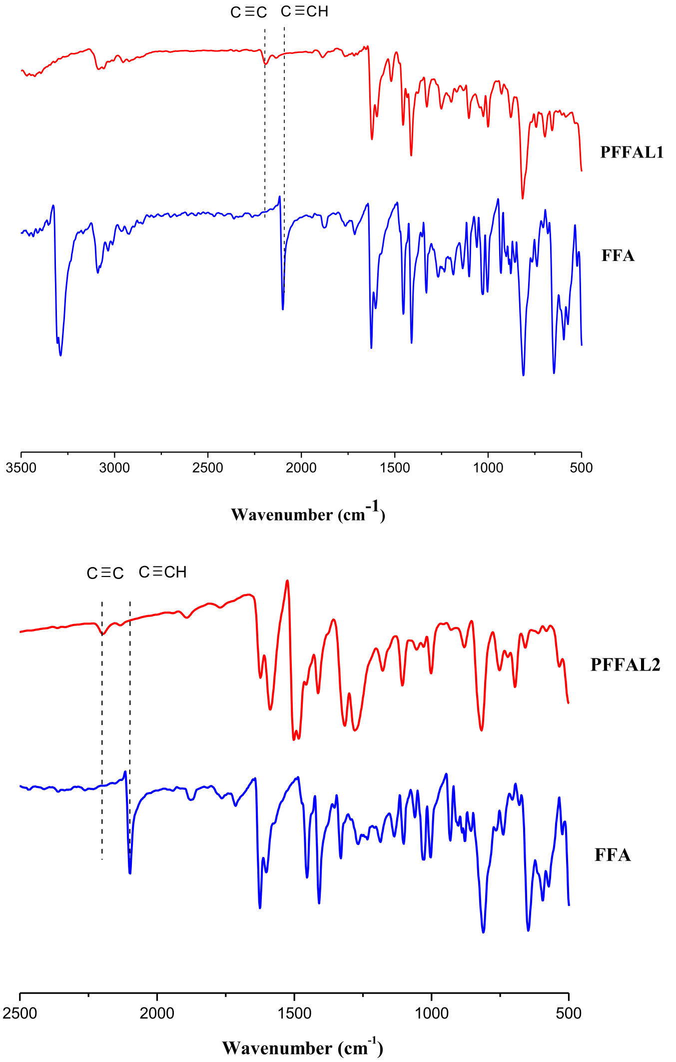

Fig. 1. Comparative IR spectra of **PFFAL1** (top) and **PFFAL2** (bottom).

Table 1
Molar masses of **PFFAL1** and **PFFAL2**, determined by SEC with poly(styrene) calibration and THF as eluent.

Polymer	$\overline{Mn}$ (g mol^{-1})	$\overline{Mw}$ (g mol^{-1})	PDI ($\overline{Mw}/\overline{Mn}$)
PFFAL1	2.3×10^4	3.0×10^4	1.3
PFFAL2	1.4×10^4	1.5×10^4	1.1

ferrocene at the half-wave potential of ($E_{pa} + E_{pc}$)/2 = 0.097 V, while **PFFAL2** displays two quasi-reversible oxidations: the ferrocene moiety is oxidized at 0.101 V and the triarylamine at 0.573 V *vs.* Fc$^+$/Fc.

To further prove the stability of these polymers as cathode materials in Li-organic batteries, electrodes were built. Due to the low intrinsic conductivity of the polymeric backbone, the electrochemical behavior of the polymer was investigated in a composite electrode. **PFFAL1**-based composite electrodes were measured in 0.1 M LiBF$_4$ in propylene carbonate solution (Fig. 4). As can be seen, owing to the presence of ferrocene moiety, cyclic voltammograms reveal reversible reactions. The potential separation between the oxidation and reduction peak is about 350 mV, which is obviously higher than that in solution and indicates the limited charge transfer within the electrode. The approximately symmetrical peaks indicate high coulomb efficiency for the charge–discharge processes and the electrochemical stability of the electroactive polymers is examined by CV measurements over 20 cycles. On repeated cycling, there is no significant change in the oxidation and reduction peak potentials or currents. Notably, **PFFAL1**-composed electrode exhibits excellent reversible redox performance in different electrolytes (SI, Fig. S5). The composite electrodes of the triarylamine-containing polymer **PFFAL2** possess similar stabilities, when the cycling is stopped at a potential of 0.5 V *vs.* Ag/AgNO$_3$ (Fig. 4). However, when cycling is extended to 1.2 V, the triphenylamine moiety is oxidized which leads to a positive charge at the free *para*-position of one phenyl ring attached to the triarylamine and enables oxidative coupling. This leads, according to the literature, to a shift and decrease of the triarylamine signal [57]. These observations demonstrate that these synthetic conjugated poly(fluorenylethynylene) type polymers could be further investigated as cathode-active materials for rechargeable lithium batteries.

3.5. Coin cell studies

The charge–discharge behavior of the prepared polymers **PFFAL1** and **PFFAL2** were further examined as cathode materials for lithium coin cells. For that reason, coin cells were prepared under inert atmosphere using a composite electrode (polymer/VGCF/PVDF, 10/80/10, *w*/*w*/*w*) as cathode and a lithium foil as anode material. A solution of 0.5 M LiClO$_4$ in propylene carbonate served as the electrolyte.

To prove the homogeneity of the composite electrodes, SEM images were taken (Fig. 5). Electrodes of both polymers show a loose, homogenous and porous morphology, which may provide sufficient surfaces for realizing efficient redox reactions of the polymeric electrodes.

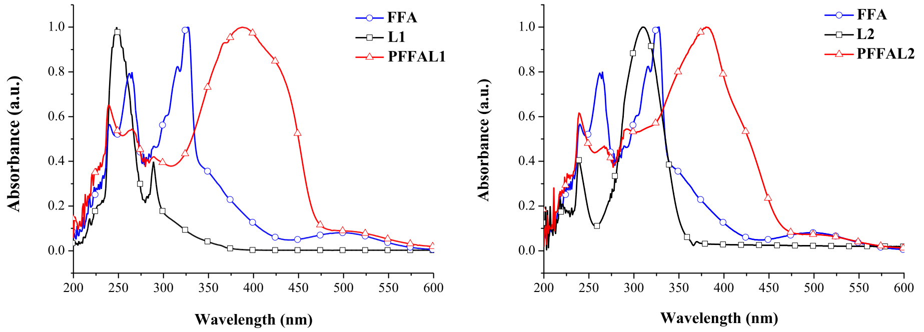

Fig. 2. Comparative absorption spectra of **PFFAL1** (left) and **PFFAL2** (right) in THF solution.

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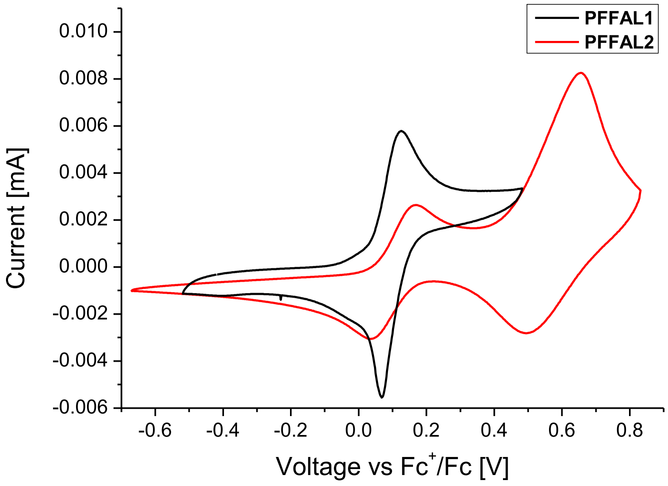

Fig. 3. Cyclic voltammograms of **PFFAL1** (black line) and **PFFAL2** (red line) in THF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of 100 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 6, **PFFAL1** exhibits at 1 C charging rate an initial discharge capacity of 52 mAh g^{-1} with a stable voltage plateau at about 3.50 V, which corresponds to 95% of the theoretical capacity of this polymer. After 100 cycles, still a discharge capacity of 48 mAh g^{-1} (88% of theoretical capacity) could be obtained, underlining the stability of this composite electrode. Even at 5 C charging rate, the discharge capacity of the first cycle is nearly identical with the one obtained at 1 C (52 mAh g^{-1}, 95% of theoretical capacity), indicating the beneficial charge transport/mobility properties of such conjugated ferrocene-containing polymers. Also here the electrode is quite stable with 46 mAh g^{-1} (84% of theoretical capacity) after 100 cycles. At 10 C the initial capacity notably decreases to 39 mAh g^{-1} (71% of theoretical capacity), but still the electrode displays stable charge/discharge curves, resulting in a discharge capacity of the 100th cycle of 36 mAh g^{-1} (66% of theoretical capacity). However, at such high currents, the mass transport is too slow, leading to polarized electrodes and consequently to a large gap between charge and discharge curves (Fig. 6).

The charge–discharge behavior of **PFFAL2** is much more complex due to the incorporated triphenylamine building block. The initial charging curve at 1 C (Fig. 6, black line) displays one plateau at about 3.5 V owing to the oxidation of the ferrocene moiety, while at about 3.8 V the oxidation of the triphenylamine building block is visible as another broad plateau. The initial charge and discharge capacity of **PFFAL2** is 100.7 and 88.5 mAh g^{-1}, respectively, which slightly exceeds the theoretical capacity (82.3 mAh g^{-1}) based on a two-electron reaction. Both the low columbic efficiency as well as the increased capacity of the first charge cycle, can be explained by the irreversible side reaction of the oxidative coupling of the triphenylamine moiety, as mentioned before [57]. During cycling, the coulomb efficiency increases to 95% (20th), and finally 98% (75th). Due to this cross-linking effect, the stability of the electrode increases, resulting in a specific capacity of 73 mAh g^{-1} (89% of theoretical capacity) after 100 cycles. Comparable to **PFFAL1**, the composite electrode of **PFFAL2** displays at 5 C a similar initial charge capacity as at 1 C (99.5 mAh g^{-1}), however, also here the initial coulomb efficiency is very low at 82%. After 20 cycles, it increases to 93%, and finally reaches 99% (50th). Again, after the first 20 cycles, the electrode is stabilized, leading to a specific discharge capacity of 54.5 mAh g^{-1} (66% of theoretical capacity) after 100 cycles. Finally, the coin cells were charged at 10 C. As also noticed for the electrodes of polymer **PFFAL2**, 10 C leads to a notable decrease of the initial charge capacity (76.4 mAh g^{-1}, 93% of theoretical capacity). Due to the higher charging speed, the

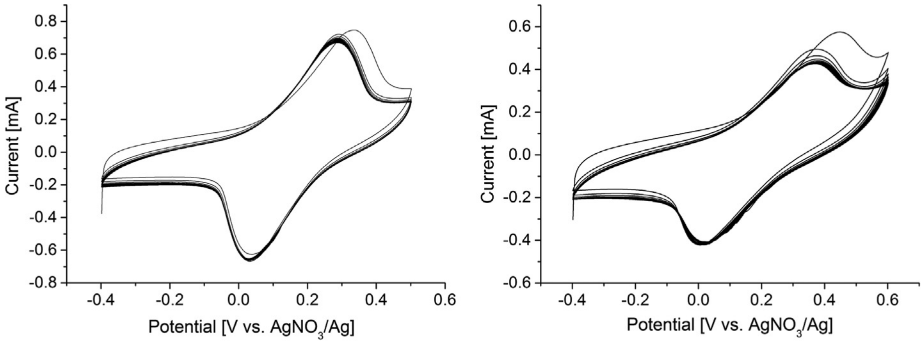

Fig. 4. Cyclic voltammograms of a polymer-composite electrode (polymer/VGCF/PVDF, 10/80/10, *w*/*w*/*w*) at a scan rate of 5 mV s^{-1} in 0.1 M $LiBF_4$ in propylene carbonate, 20 cycles; **PFFAL1** (left), **PFFAL2** (right).

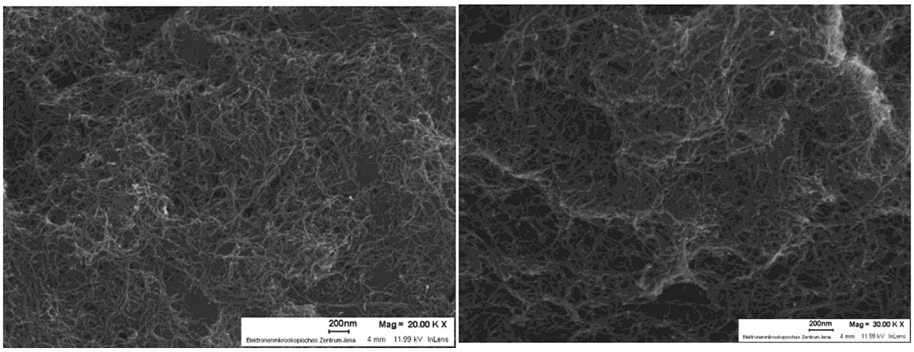

Fig. 5. SEM images of **PFFAL1**- (left) and **PFFAL2**-based (right) electrode.

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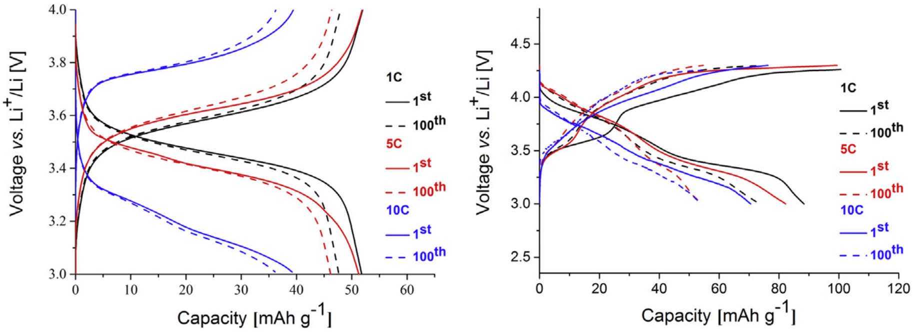

Fig. 6. 1st and 100th charging/discharging capacities of coin cells with **PFFAL1** (left) and **PFFAL2** (right) based cathode under varying charging rates.

stabilization of the electrode, that is most properly caused by cross-linking of the triphenylamine moieties, is finished not before the 40th charge-discharge cycle (Fig. 7). After 100 cycles, still 53.9 mAh g^{-1} (65% of theoretical capacity) could be discharged. This excellent cycle performance of the polymer-based coin cells may result from a combination of different favorable factors such as the stable electrochemical property of the ferrocene moiety, the poor solubility of conjugated poly(fluorenylethynylene) type structure and the homogeneous morphology of the composed electrode.

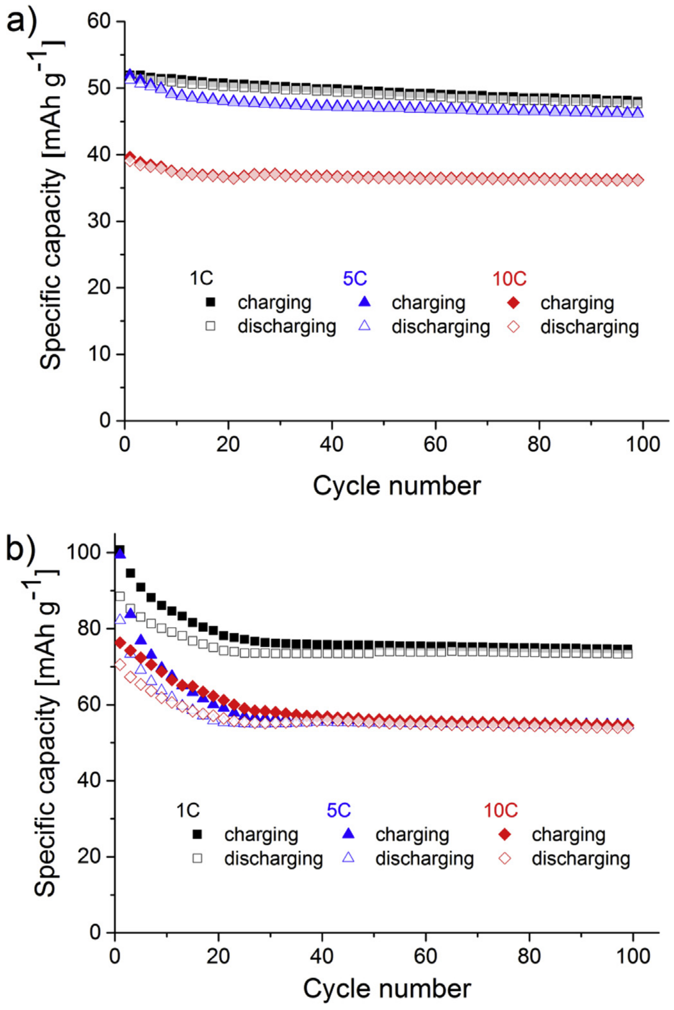

Fig. 7. Specific capacity of coin cells composed of polymer/VGCF/PVDF composites as cathode and Li as anode in 0.5 M $LiClO_4$ in propylene carbonate at different charging/discharging rates; a) **PFFAL1**, b) **PFFAL2**.

4. Conclusion

Two new conjugated poly(fluorenylethynylene) type polymers **PFFAL1** and **PFFAL2** have been successfully synthesized *via* Sonogashira cross-coupling polycondensation for charging-discharging studies as cathode materials for rechargeable lithium batteries. The ferrocene-based moiety, the conjugated redox-active poly(fluorenylethynylene) type skeleton and the homogeneous electrode surface work together and facilitate the specific capacity, rate capability and cycle endurance of the coin cells. Especially, **PFFAL1**-composed electrode retains over 90% of the initial capacity after 100 cycles at 10 C and **PFFAL2**-based cathode exhibited high utilization of the active polymer with a stable discharge capacity of 73 mAh g^{-1} at 1 C. These remarkable results demonstrate the potential of these synthetic polymers as organic cathode materials for rechargeable lithium batteries.

Acknowledgments

We are grateful to the financial support from the National Natural Science Foundation of China (project number 51373145), Hong Kong Research Grants Council (HKBU203313), Areas of Excellence Scheme, University Grants Committee of HKSAR (project No. AoE/P-03/08), Hong Kong Baptist University (FRG2/12-13/083) and the Science, Technology and Innovation Committee of Shenzhen Municipality (JCYJ20120829154440583). We also thank the Bundesministerium für Bildung und Forschung, the European Social Fund (ESF), the Thüringer Aufbaubank (TAB 2011FGR0088), and the Thuringian Ministry of Economy, Employment and Technology (TMWAT), for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.01.054.

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Please cite this article in press as: Xiang J, et al., Synthesis, characterization and charge–discharge studies of ferrocene-containing poly(fluorenylethynylene) derivatives as organic cathode materials, Polymer (2015), http://dx.doi.org/10.1016/j.polymer.2015.01.054

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