DOCTORAL THESIS

Electrofunctional ferrocene-containing metallopolymers for organic lithium-ion battery and organic resistive memory applications

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Abstract

This thesis is dedicated to developing three different types of ferrocene-containing metallopolymers for organic lithium-ion battery and organic resistive memory applications.

Chapter 1 gives an overview of organic cathode-active materials, polymeric resistive memory materials and ferrocene-containing metallopolymers. Furthermore, the previously reported applications of ferrocene-containing polymeric systems in electrochemical energy storage and electronic memory devices were also comprehensively summarized.

In chapter 2, conjugated ferrocene-containing side-chain metallopolymers **PFcFE1**, **PFcFE2**, **PFcFE3** and **PFcFE4** were designed and synthesized *via* Sonogashira cross-coupling polycondensation. The charging–discharging processes of triphenylamine-based **PFcFE1** and thiophene-modified **PFcFE4** have been successfully studied as cathode materials. **PFcFE1** composite electrode showed a capacity of 90 mAh g^{-1} and the cathode composed of **PFcFE4** retained over 90% of its initial capacity after 100 charging–discharging cycles at 10 C. These results demonstrate the huge potentials of these ferrocene-containing side-chain polymers as active cathode materials for organic lithium-ion battery applications. Besides, all prepared ferrocene-containing metallopolymers **PFcFE1**, **PFcFE2**, **PFcFE3** and **PFcFE4** also exhibited nonvolatile resistive switching behaviors with the flash memory effect of **PFcFE1**, **PFcFE2** and **PFcFE3** as well as the WORM memory

feature of **PFcFE4**, indicating the easily tunable memory properties by changing the chemical structures of the active polymeric backbone. It is also worth noting that the ITO/**PFcFE1**/Al memory device showed a high ON/OFF current ratio of 10^3 to 10^4, a low switch-on voltage of −1.0 V, a long retention time of 1000 s and a large read cycle number up to 10^5, which is superior to other reported ferrocene-containing memory examples.

Chapter 3 focuses on the development of non-conjugated ferrocene-containing copolymers **PVFVM1**, **PVFVM1-1**, **PVFVM2**, **PVFVM3**, **PVFVM4**, **PVFVM5** and **PVFVM6** based on different heteroaromatic moieties which were prepared by AIBN-initiated chain addition polymerization. The as-prepared copolymers **PVFVM1** and **PVFVM1-1** exhibited electrochemical characteristics of both ferrocene and triphenylamine pendants with reversible multiple redox waves at the half potentials of $E_{1/2}$ = –0.06, 0.30, and 0.42 V (*vs.* Fc/Fc^+). Notably, the composite electrode based on **PVFVM1** afforded a discharge capacity of 102 mAh g^{-1} at 10 C, corresponding to 98% of its theoretical capacity. The cycle endurances of the active polymer electrodes composed of **PVFVM1** or **PVFVM1-1** were both evaluated for over 50 numbers and no significant capacity reduction over cycles were observed. On the other hand, initial current–voltage results of memory devices based on **PVFVM1**, **PVFVM1-1**, **PVFVM2**, **PVFVM3**, **PVFVM4** and **PVFVM6** also revealed their great potentials in electronic information storage. The stability and reproducibility of the corresponding memory devices based on these materials will be further evaluated in the near future.

We used 1,1'-ferrocenediboronic acid bis(pinacol) ester to develop conjugated ferrocene-containing main-chain metallopolymers in chapter 4. All these rationally designed metallopolymers **FcMMP1**, **FcMMP2**, **FcMMP3** and **FcMMP4** with one or two ferrocene moieties were produced *via* Suzuki cross-coupling polycondensation. Their structural information, molecular masses, photophysical features and thermal properties have been well studied. Electrochemical performances of the formed polymers were examined to clarify their potentials as cathode-active materials for organic lithium-ion batteries. Initial current–voltage results suggested the flash memory behaviors of all the fabricated devices based on these prepared ferrocene-containing main-chain metallopolymers and thus proved their feasibilities in electronic memory devices. Their charge- and data-storage characteristics for more efficient organic battery and memory applications are under further investigation.

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