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Organometallic polymer material

for energy storage

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Ferrocene-based polymers, poly(ferrocenyl-methylsilane) and its derivative was synthesised by ring-opening polymerization. The product shows a promising cathode application in Li-ion, Na-ion and all-organic battery. The ultra-high power density, excellent cycling stability and decent capacity performance makes it comparable even superior to the conventional inorganic electrode material.

Battery with high energy density and power density has always been the biggest pursuit for scientists and it motivates us to explore alternate material or alternate battery system with new structure, new architecture and even new reaction mechanism. Nowadays, inorganic intercalation compounds and inorganic/carbon composites have been proposed and widely studied in energy storage[1,2]. Though with much development, their rigid crystal lattice greatly narrow the space for a further energy density improvement and the scaled material production incurs the sustainability issue. Hence, the green battery concept was proposed in 2008 by M. Armand and J.-M. Tarascon.[3] After that, anode or cathode applications of the organics or polymers with different function group have been fulfilled. So far, electro-active conducting polymer,[4] organ-sulfur polymers,[5] nitroxide radical,[6] aromatic carbonyl derivatives[7] has been investigated for Li^+ or Na^+ storage. Despite the merit of structural flexibility and stability, fast reaction kinetics and more adjustable electrochemical property, most of them are originally in an oxidative state and have to be coupled with Li/Na metal or other Li^+/Na^+ host. The cathode application of the organics in a "real" Li/Na-ion battery has seldom been mentioned. In addition, though the active polymer material itself can be super thermal-stable and highly oxidation-resisting, the Li/Na anode still imposes the safety concerns on the full cell. Thus, searching for more suitable cathode is crucial for the development of "green battery".

Herein, we propose the cathode application of poly(ferrocenyl-methylsilane) and its derivative. The idea originates from the unique property of ferrocene. Ferrocene, an organometallic compound, has been extensively studied as a standard electrode in electrochemical analysis because of its air stability, super-fast electrochemical response and so on.[8] However, its solubility in the organic solvent blocks its electrode application in energy storage. Using ferrocene-based polymer supplies a solution to the dilemma. Toshio Masuda

proved the viability of using the polymer with ferrocene moieties as the cathode for Li-ion batteries.[9] A decent capacity was obtained by the ferrocene polymers with carbon bridges, unfortunately the materials were still bothered by the capacity fading due to the low molecular weights (Mw: 3, 500-5, 000) and thus-resulted dissolution loss. Actually, most poly-ferrocene collected by carbon bridge bond shows limited chain length which makes the dissolution loss unavoidable. On the other hand, though poly-ferrocene with silicone or other bridge bond can have high molecular weight, they usually have a "big" function group which "dilutes" the content of ferrocene active site and make the capacity not competitive.

In this paper, we used ring-opening polymerization (ROP) to get two ferrocene-based polymers with short silicone bridge bond, poly(ferrocenyl-methylsilane) (PFS1) and poly(ferrocenyl-Chloro-propylmethylsilane) (PFS2) (see scheme S1, ESI†).[10] The silicone bridge bond enables the formation of the polymer with high molecular weight (Mw: ~80,000, determined by GPC analysis). The cathode application of the ferrocene-based polymers was demonstrated in Li-ion, Na-ion and all-organic battery. The extra merit of the film-forming property was presented and investigated. Comparing with previously reported polymer electrode material, the organometallic polymer keeps the features of flexible polymer backbone and stable structure, more importantly, its originally reductive state, super-fast reaction kinetics and general reaction mechanism greatly widens the range of anode candidates and supplies a new power-density-enhancing strategy applicable for different battery systems.

Comparison of the electrochemical behavior of PFS1 and PFS2

Reaction mechanism of the ferrocene polymers is exemplified by the PFS1 sample in Scheme 1. We can see that the ferrocene moiety is the only electro-active site in the polymer. In order to get more
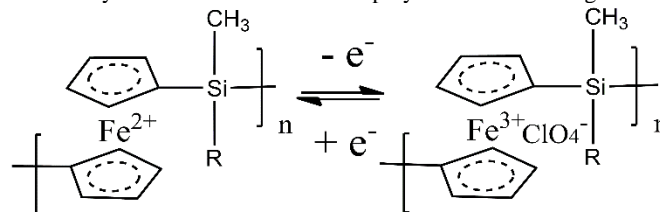
Scheme 1 Reaction mechanism of the PFS1 electrode.

information of the electrochemical behaviors of our polymers, PFS1 was first compared with PFS2 in terms of CV measurement. Fig. 1a shows the cyclic voltammograms of these two compounds in 0.1 M Tetrabutylammonium hexafluorophosphate (TBAHFP)/Dichlorome-thane (DCM) electrolyte. The two ferrocene-based polymers have very similar redox response, with two pairs of peaks locating around 0.47/0.67 V and 0.67/0.85 V vs. Hg/Hg_2Cl_2. Despite the slight difference from the typical cyclic voltammogram of ferrocene, which usually shows a pair of redox peaks centered around 0.521 $\pm$0.026 V (vs. Ag^+/Ag) in common organic electrolyte,[11] we can state that even existing as a moiety in the polymer chain, the Fe^{2+}/Fe^{3+} site still dominates the redox behavior of the ferrocene-contained polymer. The double-peaks phenomenon was widely observed in the CVs of the polyferrocene electrodes, and it has been mainly interpreted by the stepwise oxidation/reduction of the polymer, where the alternating ferrocene centers attaching to the chain are oxidized.[12] In addition, comparing the redox peaks of PFS1 and PFS2 reveals that the chloropropyl-substitution will not lead to an obviously increased redox potential. Therefore, PFS1 is considered to be a better candidate for energy storage because of its smaller monomer molecular weight. In the following, we will focus on the investigation of PFS1 and its electrochemical behavior in different battery systems and its special application in film electrode.
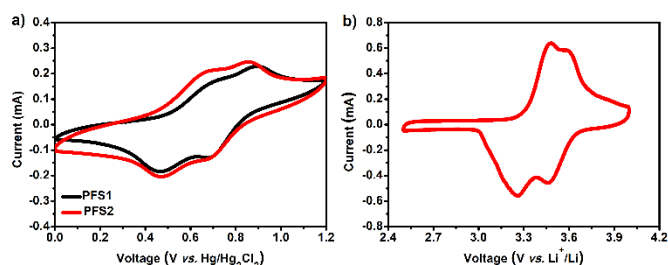

Fig.1 (a) The CV curves of the PFS1 and PFS2 electrode in 0.1 M TBAHFP/DCM electrolyte at a scan rate of 25 mV s^{-1}. (b) The cyclic voltammogram of the PFS1 electrode in 1 M $LiClO_4$/EC+DMC electrolyte, scan rate: 0.5 mV s^{-1}, potential range: 2.5-4.0 V.

PFS1 in Li-ion or Na-ion battery

According to the working mechanism illustrated in Scheme 1, the Fe^{2+}/Fe^{3+} redox pair is totally independent of Li^+ or any other cation. Thus, in principle, PFS1 can be coupled with any redox pair with a lower potential, either Li^+/Li or Na^+/Na to construct a battery.

We first screened the PFS1 electrode in different Li^+ electrolytes (Fig. S1 in ESI†). Obviously, the electrochemical behavior is greatly affected by the solvent. In 1 M LiTFSI/DOL+DME electrolyte, it shows fast capacity decay within the first 5 cycles; while in 1 M $LiClO_4$/EC+DMC electrolyte, the capacity loss greatly decreased. The dissolution of PFS1 in different solvent should be the reason, as being revealed by the yellow color of the electrolyte in the detached PFS1|1 M LiTFSI/DOL+DME|Li cell. Thus, 1 M $LiClO_4$/EC+DMC electrolyte was chosen for the further evaluation.

The CV profile of the PFS1 electrode is presented in Fig. 1b. It shows two pairs of symmetrical peaks at around 3.35 V vs. Li^+/Li. The result agrees well with that shown in Fig. 1a, and the two-pair-peaks CV signal should be also explained as being mentioned above.

The cycling performance of PFS1 cathode at 2 C rate (1 C=110 mA g^{-1}) in 1 M $LiClO_4$/EC+DMC electrolyte is displayed in Fig. 2a. It gave about 110 mAh g^{-1} capacity in the first cycle and still had about 97 mAh g^{-1} capacity after 200 cycles, indicating a very insignificant dissolution loss. Additionally, even at the 50 C rate, the PFS1 cathode still exhibited excellent capacity retention. In the inset of Fig. 2a, no capacity decay was observed after 500 cycles, further suggesting a good maintaining of reversibility. The capacity vs.

current plot was recorded at 1 C to 50 C rate (Fig. 2b). At 1 C rate, the PFS1 cathode delivered a capacity of 115 mAh g^{-1}, very close to the theoretical value of 118 mAh g^{-1}. As the rate increased, the capacity decreased remarkably slowly until it reached 90 mAh g^{-1} at 50 C rate. The result means that the PFS1 cathode can release 77% theoretical capacity within 72 s. In Fig. 2c, the voltage profiles at different rates are presented. Obviously, the increasing current rate did not lead to notably sloped discharging plateau, in another word, the average discharging voltage slightly decreased from 3.34 V at 1 C to 3.15 V at 50 C. The small voltage decay reflects the excellent power performance. The energy density and power density of the PFS1 cathode is compared with $LiFePO_4$, radical polymer and carbon capacitance material in Fig. 2d (The comparison was made on the base of the data in reference 13, 14 and 15). Though in the low-power mode, the PFS1 electrode does not show notable advantage over $LiFePO_4$; it maintains a striking energy density in the high-power mode, such as, 289 Wh kg^{-1} vs.17343 W kg^{-1}. The surprisingly good energy/power density is superior to all other polymer electrodes or capacitance material and even comparable to the radical polymer. Certainly, the fast reaction kinetics of the Fe^{2+}/Fe^{3+} redox should be accounted for the excellent rate capability, which has been widely witnessed by the ferrocene electrode.[16]
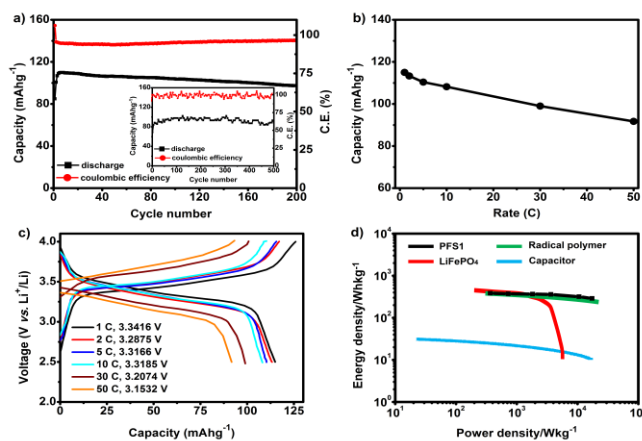

Fig. 2 (a) Cycling performance of the PFS1 electrode at 2 C rate, the inset is the long-term cycling stability at 50 C rate; (b) Discharge capacity vs. C-rate of the PFS1 cathode; (c) Voltage profiles of the PFS1 cathode at different C-rates, the average discharging voltage is also presented (1 C=110 mA g^{-1}); (d) Comparison of the power density vs. energy density of PFS1, $LiFePO_4$,[13] radical polymer[14] and capacitance.[15]

The working mechanism enables the cathode application of polyferrocene material in Li as well as Na ion battery, so we further tested the PFS1 electrode in 1 M $NaClO_4$/EC+DMC electrolyte, the charge/discharge plot is shown in Fig. S2 (ESI†). In summary, the PFS1 electrode presents the similar electro-reactivity in Na^+ electrolyte as in Li^+ electrolyte. The result well meets our expectation because of the same reaction principle of PFS1 electrode in different electrolyte.

PFS1 in all-organic battery

The cathode application of the PFS1 electrode can be extended to other systems, such as all-organic battery because of its originally reductive state. Here, we show an example of the all-organic battery with PFS1 cathode and Poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-c:4,5-c`] dipyrrole-2,6(1H,3H)-diyl)-1,4- phenylene] (PMDA) anode (see the supporting information for PMDA preparation). The voltage profile of PMDA anode is shown in Fig. S3 (ESI†). Fig. 3a shows the 5th charge/discharge curve of the PMDA|1 M $NaClO_4$/EC+DMC

|PFS1 cell, the average discharge voltage is around 1.2 V with a rather flat charge/discharge plateau, corresponding with the average working voltage of 2 V for PMDA anode and 3.2 V for PFS1 cathode. In Fig. 3b, the cell delivered 85 mAh g^{-1} capacity in the first cycle, and the coulombic efficiency of 86% indicates a small irreversible capacity loss. After 200 cycles, the cell still released a discharge capacity of 63 mAh g^{-1}, with the capacity retention higher than 74%. The stable cycling should be explained by the excellent structural stability of the PFS1 and PMDA polymer electrode. It can be expected that the energy density can be further enhanced if the organic anode with lower redox potential can be adopted, such as recently reported Na$_2$C$_8$H$_4$O$_4$.[17] Anyway, here, we demonstrate an all-organic battery with decent capacity performance and excellent cycling stability.
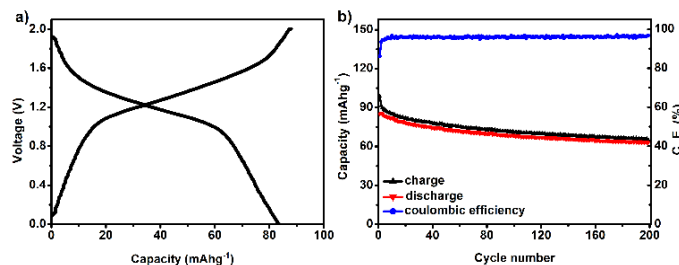

Fig. 3 (a) The 5th charge/discharge curve and (b) the cycling stability of the PMDA|1 M NaClO$_4$/EC+DMC|PFS1 cell, current rate: 5 C.

PFS1 membrane electrode

Another merit of PFS1 material is its film-forming ability, which means a free-standing electrode can be obtained. The preparation of the PFS1 film is described in the supporting information. Briefly, PFS1 was dissolved into methylbenzene/dichloromethane (5:1, v/v) mixture solvent, then the mixture solution was slowly dropped into distilled water. After the solvent evaporation, a yellow film could be obtained. The PFS1/carbon (Printex XE2) film was also obtained by a similar procedure (see the ESI†). The SEM images of PFS1 and PFS1/carbon films are shown in Fig. 4a and 4b, respectively. The films are smooth and without crack. The PFS1/carbon film was preliminarily examined by the CV test and the result is shown in Fig. 4c. The redox behavior of the PFS1/carbon film is essentially the same as the PFS1 powder electrode, proving the feasibility of the PFS1/carbon membrane electrode. Further attempt should be focus on all-organic film battery, such as PMDA film/PFS1 film. This work is still in progress in our group.
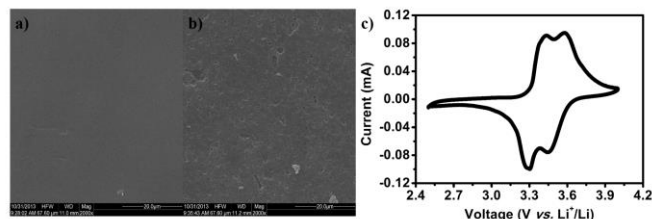

Fig. 4 The SEM images of (a) PFS1 film and (b) PFS1/carbon film; (c) The CV plot of the PFS1/carbon film electrode at the scan rate of 1 mV s^{-1} in the potential range of 2.5-4.0 V.

Conclusions

In summary, PFS1 material with high molecular weight, was obtained by the ROP method. The originally reductive state of PFS1 enables its cathode application in a "real" Li-ion or Na-ion battery and all-organic battery. Electrochemical tests show that the PFS1 electrode can deliver a capacity of 115 mAh g^{-1} at 1 C rate in Li$^+$ electrolyte. The material also shows an excellent cycling stability

and strikingly good rate capability. PMDA/PFS1 all-organic battery has been fabricated and it exhibits a decent capacity and very stable cycling. Preliminary investigation on PFS1/carbon film proves its potential application in membrane electrode. The work here supplies a new strategy for high power/energy density battery.

Notes and references

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