Supporting information

Organometallic polymer material for energy storage

Hai Zhong[a], Guofeng Wang[a], Zhiping Song[a,b], Xiang Li[a], Hongding Tang[a], Yunhong Zhou[a], Hui Zhan[a*]

1. Material synthesis

1.1 Poly(ferrocenyl-methylsilane) (PFS1)

The preparation of PFS1 is as following. Ferrocene (3.75 g, 20 mmol), tetramethylethylenediamine (TMEDTA) (6 ml, 40 mmol), n-BuLi (20 ml, 50 mmol) and petroleum ether (120 ml) were put into Schlenk reaction flask and stirred for 48 h to get a yellow dilithio-salt precipitate. After filtration and being washed three times with petroleum ether, the yellow solid was gained. It was added in 100 ml petroleum ether, then 2.1 ml dichloromethylsilane was added to the mixture under -20 °C ice-bath. After being stirred for 24 h, the liquid was collected by filtration. The liquid was heated to remove most solvent, and the obtained solid was vacuum dried to get the red-orange precursor. A copolymerization treatment is performed on the precursor at 150 °C in vaccum for 4 h. The solid was further purified by three times extraction in tetrahydrofuran and methanol to obtain the final orange-yellow product.

All the solvents were distilled before use.

PFS1 ^{1}H-NMR ($CDCl_3$, 300 MHz): δ= 0.43 (s, 3H, Si-CH_3), 4.22-4.40 (br, 8H, Cp), 4.69 (s, H, Si-H).

PFS1 FT-IR (KBr, cm^{-1}):3089, 2961, 2835, 2247, 1732, 1462, 1421, 1383, 1366, 1256, 1167, 1037, 911, 776, 734, 648, 631, 459.

1.2 poly(ferrocenyl-Chloropropylmethylsilane) (PFS2)

The preparation of the PFS2 sample is similar to that of the PFS1 sample, except chloropropylmethyldichlorosilane instead of dichloromethylsilane was used as one of the raw material to introduce Cl group.

PFS2 1H-NMR (CDCl3, 300 MHz) δ [ppm]: 0.47(s, 3H, CH3), 0.99(t, 2H, SiCH_2), 1.80(m, 2H, CH_2), 3.50(t, 2H, CH_2Cl), 3.96-4.22(br, 8H, Cp).

PFS2 FT-IR (KBr, cm^{-1}): 3087, 2952, 1725, 1420, 1382, 1300, 1251, 1163, 1036, 776, 677.

1.3 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)

We chose pyromellitic dianhydride (PMDA) and p-phenylenediamine (pPDA) as the starting materials. Equimolar PMDA reacted with pPDA under reflux in NMP solvent for 6 hours; the precursor was filtrated, washed with ethanol, dried at 120°C for 12 hours, then heated in N_2 flow for 8 hours at 300 °C. The final product is yellow powder, and the yield is 99%.

1.4 PFS1 film

In order to get the PFS1 film, we dissolved PFS1 into methylbenzene/ dichloromethane (5:1, v/v) mixture solvent, then slowly dropped the solution into distill water. Due to the different solubility of PFS1 in water and the mixture solvent and the low density of PFS1, PFS1 deposited as a membrane on the surface. After naturally evaporating the solvent, a yellow film could be obtained.

1.5 PFS1/carbon film

Printex Carbon (Printex XE 2) was dried and well milled before use, then accurately weighed Printex carbon was transferred into a plastic tube, and the methylbenzene/dichloromethane (5:1, v/v) mixture solvent was added. A homogeneous carbon suspension was obtained after 60 min ultra-sonication. After mixing the carbon suspension with PFS1 in methylbenzene/dichloromethane solution, repeated the procedure in 1.4, a black PFS1/carbon film could be obtained.

2. Electrochemical test

The cathodes were prepared by mixing 40 wt.% active material with 40 wt.% conductive carbon (PRINTEX XE2) and 20 wt.% polytetrafluoroethylene (PTFE) binder and then pressing the mixture on a stainless steel mesh. The electrodes were dried at 100 °C before use. Three different anodes were used for different battery system. Li or Na foil anode was used for Li or Na secondary battery respectively, 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) was used as the anode for all-organic battery. 2016 coin cells were fabricated in an argon-filled glove box (Mbraun, Germany). The cathode and the anode were separated by a Celgard 2300 separator. 1 M $LiClO_4$ dissolved in 1:1 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC) was used as the electrolyte for Li battery, and 1 M $NaClO_4$ dissolved in 1:1 (v/v) EC/DMC was used as the electrolyte for Na battery. The charging/discharging tests were conducted on Land battery cycler (Land Co. Ltd., China). Cyclic voltammetry (CV) measurements were carried out on CHI660 Electrochemical Workstation. A three-electrode cell was used in CV tests, experiment conditions varied with the specific requirement. For example, in the study of the redox behavior of PFS1 in Li^+ electrolyte, the PFS1 electrode was used as the working electrode, and Li foil was used as the counter and the reference electrode.

3. Energy density and power density calculation:

Energy density: $W = \frac{C \times U}{m}$ (Wh kg^{-1})

Power density: $P = \frac{w}{t} = \frac{C \times U}{t} = \frac{It \times U}{t} = IU$ (W kg^{-1})

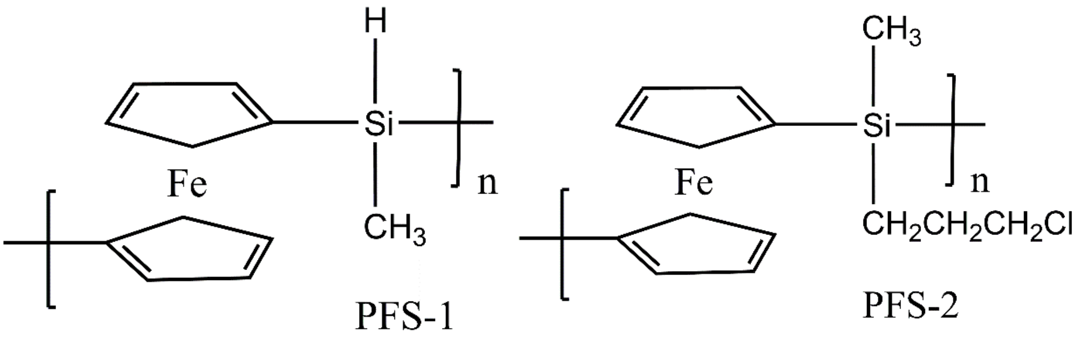
C----Discharge capacity (mAhg^{-1})

U---- Average discharging voltage (mAhg^{-1})

m---- Active material weight (g)

t ----The discharging time (s)

I ---- Discharge current (mA)



M_{PFS-1} = 228 g·mol^{-1} M_{PFS-2} = 305 g·mol^{-1}

Theoretical capacity： 117.5 mAh·g^{-1} Theoretical capacity： 87.9 mAh·g^{-1}

Scheme S1 The molecular structures of PFS1and PFS2.

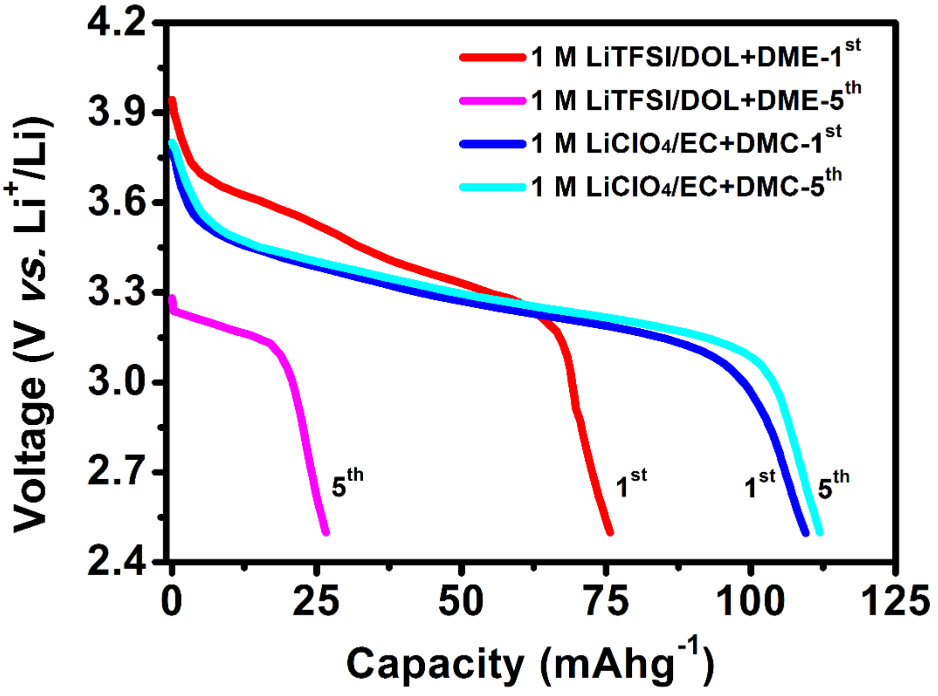


Fig. S1 The discharge curve of PFS1 electrode in two different Li^+ electrolyte.

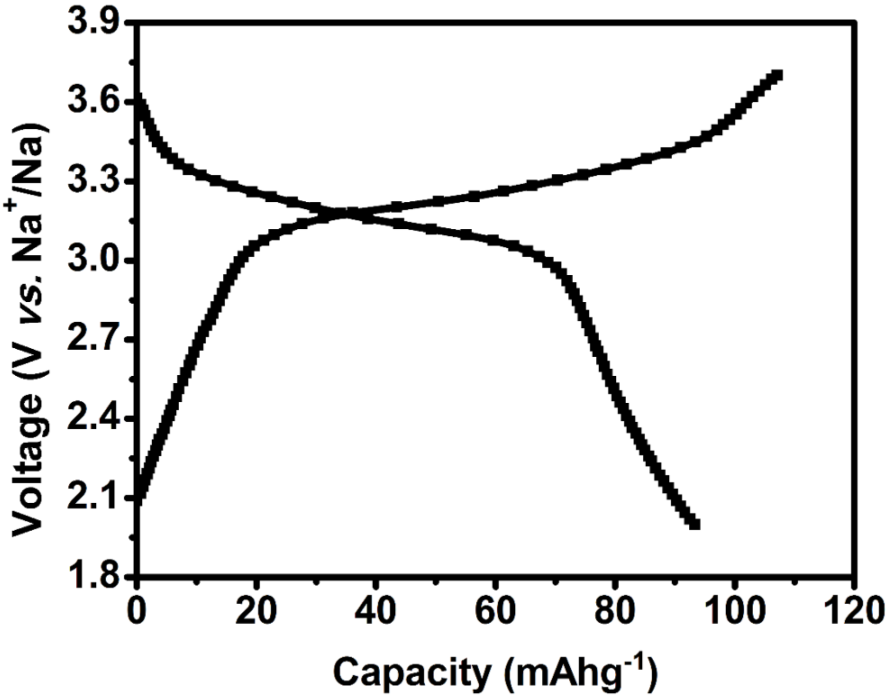


Fig. S2 The charge/discharge profile of PFS1 electrode in 1 M $NaClO_4$/EC+DMC electrolyte.

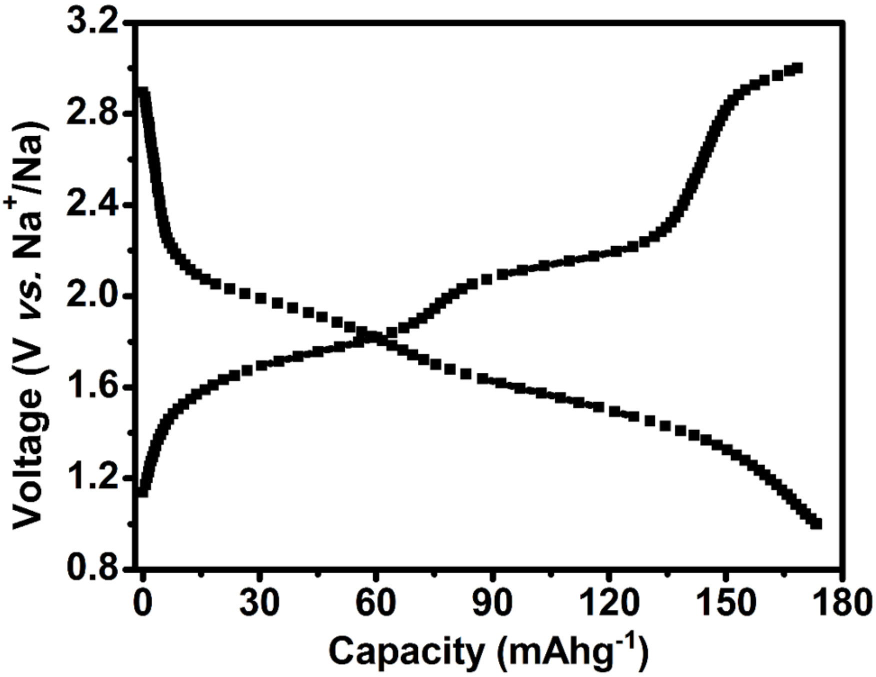


Fig. S3 The charge/discharge profile of the PMDA electrode in 1 M

$NaClO_4$/EC+DMC electrolyte.

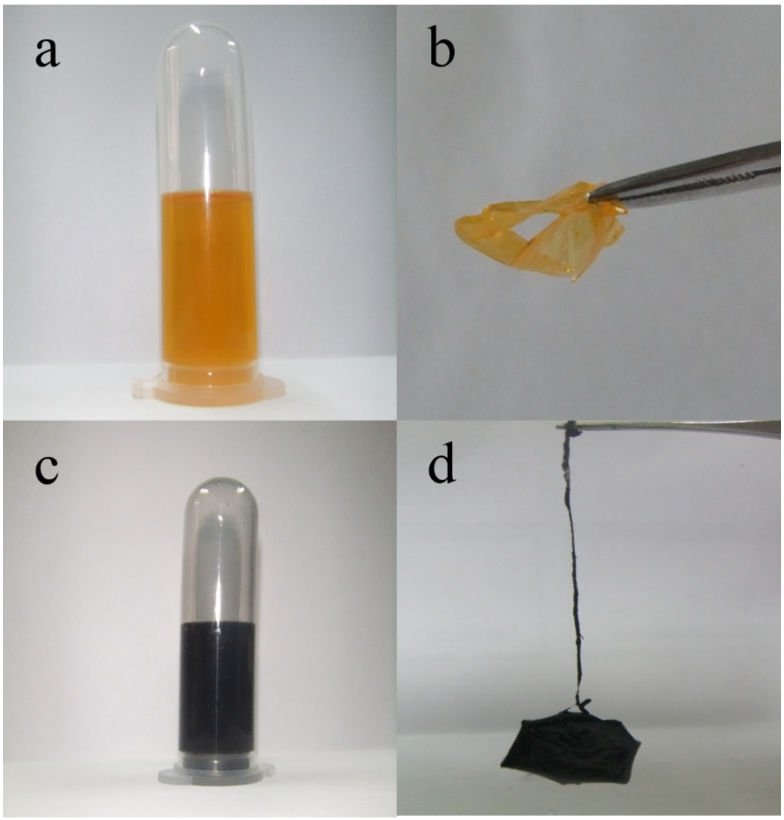


Fig. S4 PFS1 solution (a) and film (b) and PFS1/carbon (c) suspension and film (d).