

Supporting Information

One-pot *in situ* redox synthesis of hexacyanoferrate/conductive polymer hybrids as lithium-ion battery cathode

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Materials and Methods

The chemicals used, including silver nitrate, lithium chloride, potassium ferricyanide, pyrrole, 70,000 MW poly(sodium 4-styrenesulfonate) (PSS), polyvinyl pyrrolidone (PVP) and pentyl acetate, were all purchased from Sigma-Aldrich and used as received. All reagents used were analytical grade.

(a) Synthesis of $\text{Li}_3\text{Fe}(\text{CN})_6$ Precursor

As $\text{Li}_3\text{Fe}^{\text{III}}(\text{CN})_6$ is not commercially available, commercially available $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ was used to prepare a 0.2 M solution of $\text{Li}_3\text{Fe}^{\text{III}}(\text{CN})_6$ precursor. 50 mL of the solution was added to 50 mL of 0.8 M AgNO_3 solution under vigorous stirring for 2 h. A bright orange $\text{Ag}_3\text{Fe}^{\text{III}}(\text{CN})_6$ precipitate was formed. After the reaction, the suspension was centrifuged and washed with de-ionized water and the residue was collected. The residue was re-suspended in 100 mL of de-ionized water after washing. 100 mL of a 0.6 M LiCl solution was then introduced with vigorous stirring for another 2 h. A lime green suspension was obtained. The suspension was centrifuged and filtered to obtain the yellow supernatant $\text{Li}_3\text{Fe}^{\text{III}}(\text{CN})_6$ (~ 50 mM). The white residue of AgCl was disposed.

(b) Synthesis of Pure Li-PB and polypyrrole reference material

Reference was taken from Ming *et al.*²⁰ on potassium PB for the synthesis of pure lithium PB. 3 mL of 1.0 M HCl and 27 mL of 50 mM $\text{Li}_3\text{Fe}(\text{CN})_6$ precursor were added to a 30-mL

Teflon vessel. 3.5 g of PVP was added as a reducing agent and as a surfactant. The vessel was placed in a pressure-resistant stainless steel container, and was autoclaved at 120°C for 24 h and left to cool. The precipitate, which was of a characteristic dark blue color (LiPB), was then washed and centrifuged with de-ionized water and then with ethanol. The supernatant was disposed. The washed LiPB material was dried at 80°C for 48 h. PPy polymers were synthesized via oxidation of pyrrole monomers with APS in a 1:1.25 molar ratio, in accordance to an experimental protocol reported by Huang et al.²¹

(c) Wet-chemical synthesis of LiPB-PPy-PSS hybrid

For the synthesis of LiPB-PPy-PSS hybrid, 15.5 µL of pyrrole and 0.5 g PSS were added into a 30-mL Teflon vessel together with 3 mL of 1.0 M HCl and 27 mL of 50 mM $\text{Li}_3\text{Fe}(\text{CN})_6$ precursor. The vessel was placed in a pressure-resistant stainless steel container, and was autoclaved at 120°C for 24 h and left to cool. The precipitate, which was of a characteristic dark blue color (LiPB-PPy-PSS hybrid), was then washed and centrifuged three times with de-ionized water and then with ethanol. The supernatant was disposed. The washed LiPB-PPy-PSS hybrid material was dried at 80°C for 48 h. A hybrid material (LiPB-PPy) was also similarly prepared without the addition of PSS.

(d) Characterization

All SEM and EDX images were taken with a JSM-7400F scanning electron microscope. Powder XRD patterns were obtained from PANalytical X'pert PRO Material Research Diffraction system. FTIR spectra were recorded on a Digilab FTS 7000 Series FTIR Spectrometer. TEM images were obtained with a FEI Tecnai G² F20 electron microscope. Samples for TEM studies were prepared by placing a droplet of the sample's solution onto a copper grid coated with a thin carbon film, followed by evaporation in air at room temperature.

(e) Electrochemical Measurements

The LiPB-PPy-PSS working electrode was prepared by mixing, in pentyl acetate, the PB-PPy-PSS hybrid material with carbon black and polytetrafluoroethylene (PTFE) binder at a weight ratio of 60:30:10. Electrochemical performance measurements were conducted using 2032-coin cells. The working cathodes were prepared by pressing thin films (containing

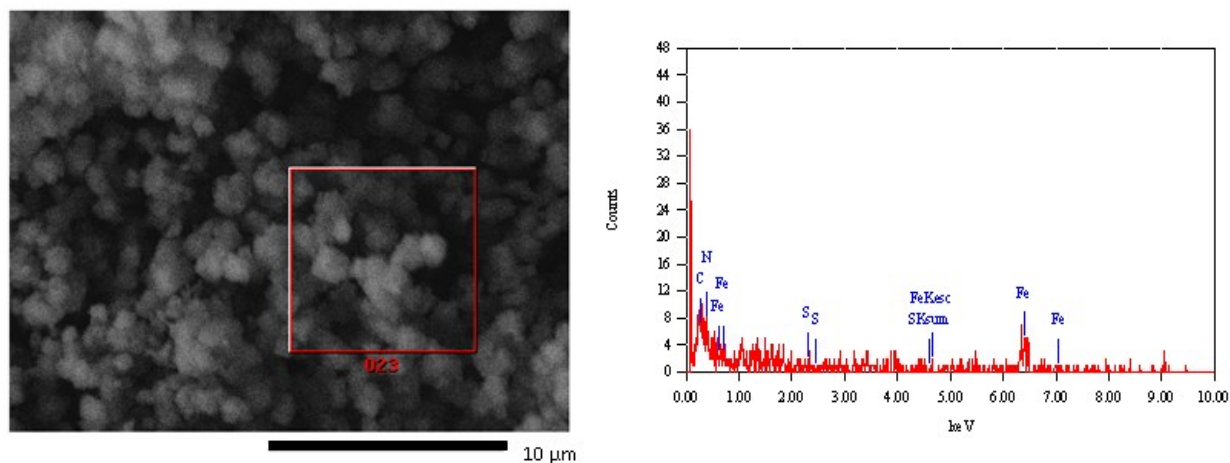
electrode material) in between two pieces of aluminum wire gauzes. The cathodes were subsequently dried overnight at 80°C to remove the residual solvent. The anode was a disk of lithium metal, and the electrolyte used was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) at a EC/DMC/EMC volume ratio of 1:1:1. Battery cells were assembled in an argon-filled glove box, and the galvanostatic charge-discharge experiments were conducted with an Arbin BT2000 testing system at various rates between 1.5 V and 4.4 V at room temperature.

Results

EDX of the hybrid material showed the presence of ~ 2% sulfur (Fig. S1), indicating the incorporation of PSS into the LiPB-PPy-PSS hybrid. PSS was able to serve as a dopant for conductive polymers,^{18, 19} increasing the conductivity and improving the performance of the LiPB-PPy-PSS hybrid as compared to the LiPB-PPy hybrid. XPS further confirmed the presence of sulfur (Fig. S2). A characteristic peak at 160–170 eV was attributed to the incorporation of PSS in the hybrid material.

The described synthesis method was extended to EDOT and Thio (Fig. S3). Similar multifaceted cubic structures were obtained. The performance of these hybrids was similarly found to be stable over 20 cycles at a charge-discharge rate of 20 mAh/g (Fig. S4).

LiPB-PPy hybrid was characterized by XRD (Fig. S5). LiPB-PPy-PSS and LiPB-PPy showed characteristic diffraction peaks at $2\theta = 17.43^\circ, 24.72^\circ, 35.21^\circ$ and 39.53° , which could be indexed to the [200], [220], [400] and [420] planes of the cubic PB structure.



Element	keV	Mass %	Counts	Error	Atomic %	X
Carbon	0.277	14.66	21.69	0.04	40.93	0.4159
Nitrogen	0.392	3.74	9.85	0.23	8.96	0.2338
Sulfur	2.307	2.54	8.08	0.60	2.65	0.1930
Iron	6.398	79.06	48.62	0.12	47.46	1.0000
Total		100.00			100.00	

Fig. S1 EDX analysis of the LiPB-PPy-PSS hybrid, showing the presence of carbon, nitrogen, sulfur and iron in the material.

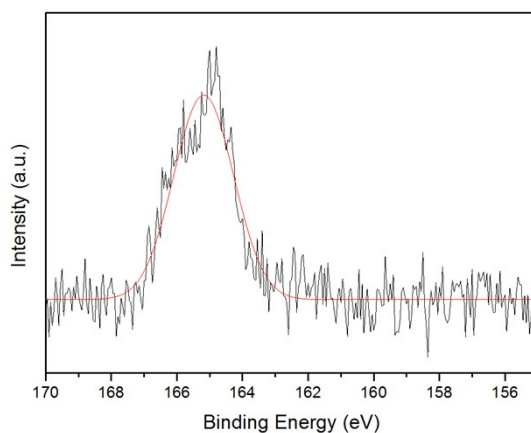


Fig. S2 XPS spectrum of the LiPB-PPy-PSS hybrid, showing the presence of sulfur in the material.

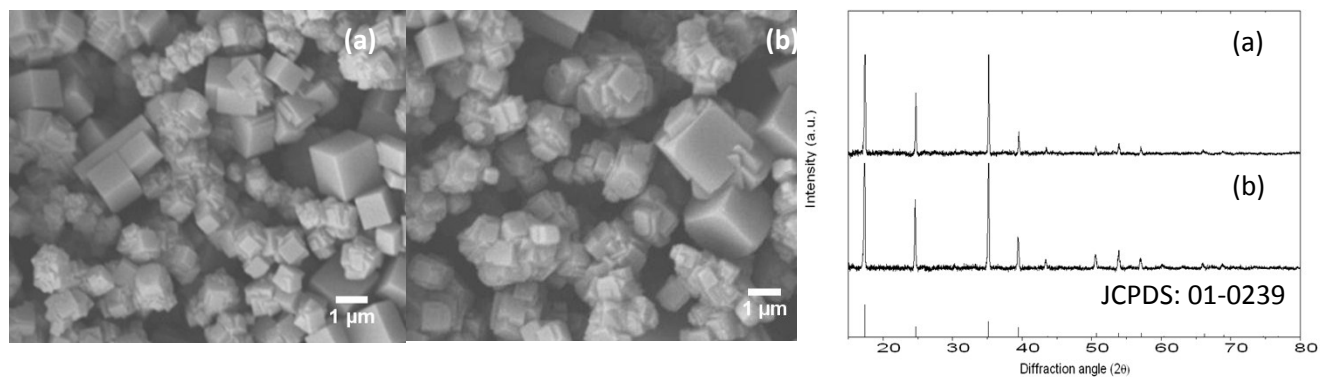


Fig. S3 SEM images (left) and XRD patterns (right) of (a) LiPB-EDOT-PSS hybrid and (b) LiPB-Thio-PSS hybrid. These two hybrid materials also showed a similar multifaceted cubic structure as LiPB-PPy-PSS (Fig. 1(a)).

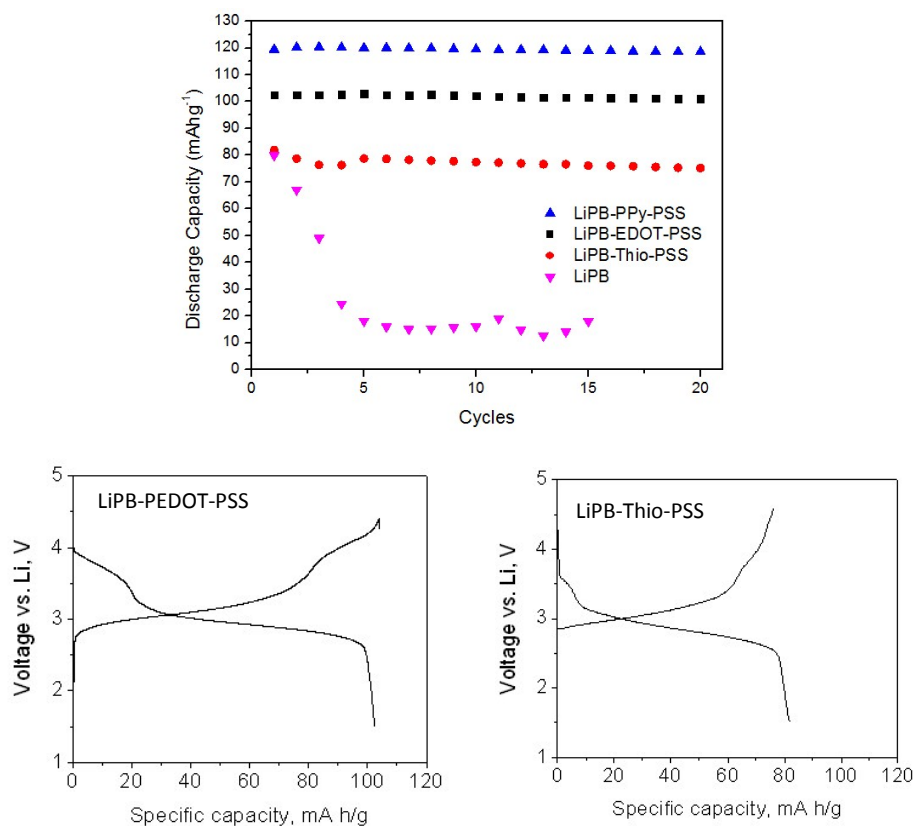


Fig. S4 Charge-discharge performance of LiPB-PPy-PSS, LiPB-EDOT-PSS and LiPB-Thio-PSS cathodes.

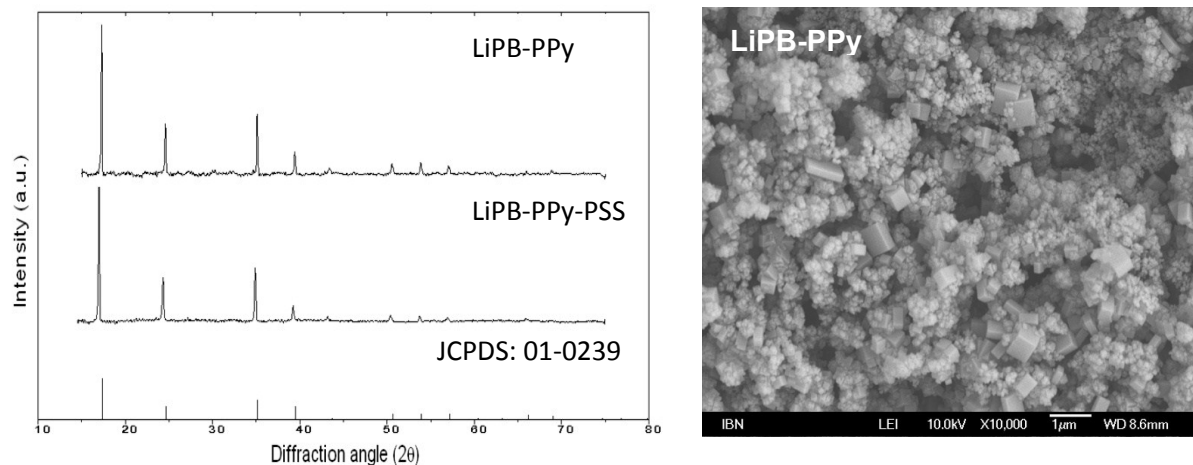


Fig. S5 (Left) XRD patterns of LiPB-PPy-PSS and LiPB-PPy hybrids. (Right) SEM image of LiPB-PPy hybrid.

	Element	Weight %
CHNS Elemental Analysis	Carbon	12.26
	Hydrogen	3.02
	Nitrogen	13.54
	Sulfur	1.39
ICP Analysis	Lithium	1.23
	Iron	9.23

Table S1 CHNS elemental analysis of LiPB-PPy-PSS hybrid indicates a PSS content of ~ 8 weight % (based on the sulfur content). A Li:Fe mole ratio of ~ 1:1 was determined by ICP analysis. The sample was digested with HNO₃/HCl and topped up to 10 mL with H₂O. Due to the poor solubility of PB compounds, precipitation was observed prior to analysis, which could have led to some uncertainty in the elemental analysis results.