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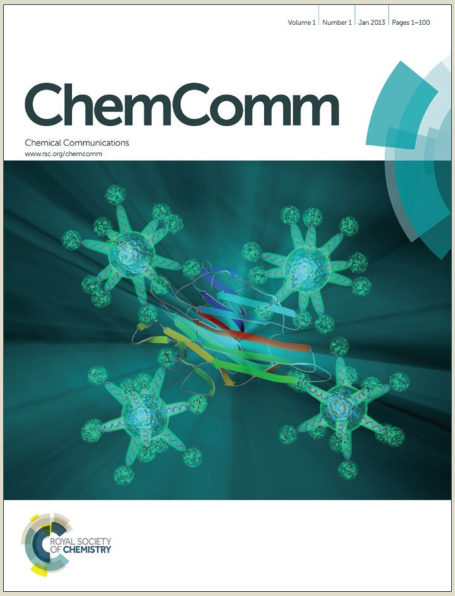

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Communication

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

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An efficient and adaptable method is demonstrated for the synthesis of lithium hexacyanoferrate/conductive polymer hybrids for Li-ion battery cathodes. The hybrids were synthesized via a one-pot method, involving a redox-coupled reaction between pyrrole monomers and $Li_3Fe(CN)_6$ precursor. The hybrids showed much better cyclability relative to reported Prussian Blue (PB) analogs.

Metal-organic frameworks (MOFs) are a broad class of porous materials that can be readily self-assembled from their corresponding metal ions and/or metal-containing clusters with suitable organic linkers.[1] The performance of MOFs in applications, such as gas storage[2-4] or their ability to host a wide variety of aqueous or non-aqueous solvent molecules for energy applications, compares favorably with zeolites.[5, 6] This is due to the presence of tunable and open channels that allow for rapid insertion of species, such as metal ions and hydrogen, into the MOF host structures.[7, 8] Recently, some MOFs, such as metal hexacyanoferrates, have received considerable attention for battery applications because of their excellent electrochemical activity, low cost and stability derived from the coordinated covalent structure.[8] In contrast to cyanide compounds, hexacyanoferrates are not hazardous for human health, and even have medical applications.[9] The zeolite-like hexacyanoferrates' ability to intercalate alkali metal cations in highly reversible redox reactions upon charging and discharging has rendered Prussian Blue (PB) and their analogs as potential electrode materials for battery applications. Zinc, copper, nickel and chromium hexacyanoferrates have been explored for use as a cathode material mainly in potassium-ion PB batteries.[7, 8, 10-12] Most recently, copper hexacyanoferrate synthesized via a co-precipitation method was found to have long cycle life and good efficiency when tested at high discharge rates in a flooded three-electrode potassium cell.[7] However, PB-based materials were reportedly unsuitable for Li intercalation/deintercalation in lithium batteries as the Li insertion/extraction into PB films tended to destroy the lattice structure,[13] leading to a rapid capacity decrease of more than 30% after only 10 cycles.[14] The high solubility of the redox intermediates as well as the difficulty in controlling bulk precipitation synthesis methods further increases the challenge of using PB as a Li-ion battery cathode material.

One promising strategy to enhance battery cyclability and improve electrochemical performance is to utilize conductive polymers to form hybrid materials. Since the discovery by Shirakawa *et al.* that virgin polyacetylene can be reversibly oxidized and reduced,[15, 16] other conducting polymers such as polythiophene, polyaniline, polyphenylene and polypyrrole[17] have been investigated for their ability in charge storage. The ability of the conducting polymers to serve as potential battery electrode materials is due to the polymer doping/undoping process, where the redox state and electronic conductivity is raised during the ion insertion process (doping). To maintain the electroneutrality of the materials, charge-compensating ions move into the polymer, making conductive polymers both an electronic and ionic conductor.

Herein we reported an efficient one-pot *in situ* wet chemical synthesis for PB-polypyrrole hybrid material, which demonstrated significantly enhance cyclability of PB when applied as cathode materials in lithium-ion battery. In this novel approach, pyrrole (Py) was polymerized by $Li_3[Fe(CN)_6]$ (used as a precursor), and poly(sodium 4-styrenesulfonate) (PSS) was added to act as both a surfactant and a dopant[18, 19] during the synthesis. The lithium PB (LiPB)-based hybrid obtained has a nominal formula, $LiFe^{III}Fe^{II}(CN)_6$-PPy-PSS (denoted as LiPB-PPy-PSS). The LiPB-PPy-PSS hybrid has a superior cyclability to LiPB, which could be attributed to the function of polypyrrole (PPy) as a host matrix and a binder to prevent dissolution of LiPB intermediates during charging and discharging. This facile one-pot *in situ* redox chemistry approach is also successfully applied to synthesize other LiPB-conductive polymer hybrids, such as polythiophene and poly-3,4-ethylenedioxythiophene (EDOT). The reported approach involves relatively mild synthesis conditions and can be easily scaled up. To the best of our knowledge, this is the first demonstration of a one-pot synthesis of hexacyanoferrate/conductive polymer hybrids and their application as cathode in lithium-ion battery with significantly improved cyclability and discharge capacity.

As $Li_3Fe(CN)_6$ is not commercially available, commercially available $K_3Fe(CN_6)$ was used to prepare a 50 mM solution of $Li_3Fe(CN)_6$ (see supporting information). The synthesis of pure lithium PB was adopted from the synthesis of potassium PB published by Ming *et al.*[20] Briefly, 3 mL of 1.0 M HCl and 27 mL of 50 mM $Li_3Fe(CN)_6$ 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 120ºC 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 80ºC for 48 h.

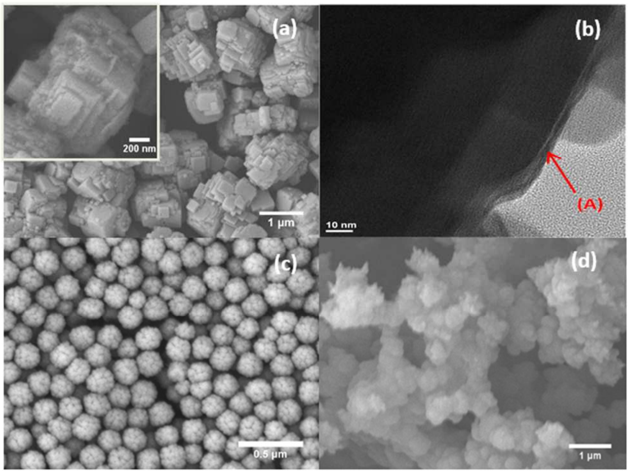

Fig. 1 (a) SEM of LiPB-PPy-PSS hybrid. (b) TEM of LiPB-PPy-PSS hybrid with polymeric layer on surface (A). (c) SEM of pure LiPB. (d) SEM of polypyrrole.

For the synthesis of LiPB-PPy-PSS hybrid, 15.5 µL of pyrrole monomers and 0.5 g of PSS were added in place of PVP. The vessel was then autoclaved at 120ºC for 24 h. The dark blue LiPB-PPy-PSS hybrid was washed and dried at 80ºC. Another hybrid material, LiPB-PPy, was also prepared without the addition of PSS. Polypyrrole polymers were synthesized via oxidation of pyrrole monomers with ammonium persulfate (APS) at a 1:1.25 molar ratio, based on the experimental protocol reported by Huang *et al.*[21]

The scanning electron microscopy (SEM) image of the as-prepared sample (Fig. 1(a)) shows a multifaceted cubic morphology and a size of ~ 1–3 µm. Pure LiPB was found to be ~ 150 nm with a spherical morphology (Fig. 1(c)). PPy polymers have a branched, amorphous structure (Fig. 1(d)). The presence of polymers such as PSS or PPy during PB crystal growth of the LiPB-PPy-PSS hybrid could provide a chemically and spatially confined and stabilized environment for the controlled growth of nanoparticles,[22] resulting in a multifaceted cubic hybrid material. The presence of PPy-PSS polymeric layer on the PB surface was confirmed by energy dispersive X-ray spectrometry (EDX) attached to the SEM, X-ray photon electroscopy (XPS) and carbon, hydrogen, nitrogen and sulfur (CHNS) elemental analysis (see Figs. S1 and S2 and Table S1 in supporting information). EDX and CHNS elemental analysis showed the presence of trace sulfur that could be attributed to the incorporation of PSS into the hybrid surface. The hybrid was further visualized by transmission electron microscopy (TEM) (Fig. 1(b)). Inductively coupled plasma (ICP) analysis (Table S1 in supporting information) indicated a Li-Fe ratio of ~ 1:1. An electron diffraction pattern could not be obtained because the PB structure was unstable under electron irradiation.

The Fourier-transform infrared (FTIR) spectrum of the as-prepared LiPB-PPy-PSS hybrid showed several peaks due to the incorporation of PPy and PSS into the PB structure (Fig. 2). The characteristic peak at 2094 cm^{-1} corresponded to the presence of C≡N stretch, which confirmed the incorporation of hexacyanoferrate into the hybrid material. The broad band at 3200 cm^{-1} was indicative of water associated with the PB structure. The presence of several peaks in the 1200 cm^{-1} region was ascribed to the in-plane C-H deformation and aryl in-plane C-N stretching vibrations of the doped state of PPy.[23] Peaks at 1411 and 1608 cm^{-1} were ascribed to the aromatic C=C stretch of PPy and PSS. The retention of the metal-organic PB crystal framework within the LiPB-PPy-PSS hybrid was validated by X-ray diffraction (XRD). The powder XRD pattern of the LiPB-PPy-PSS hybrid showed characteristic diffraction peaks at 2θ = 17.43º, 24.72º, 35.21º and 39.53º, which could be indexed to [200], [220], [400] and [420] planes of the cubic PB structure (JCPDS Card No. 01-0239). Figure 3 shows a summary of the proposed schematic for the formation of the LiPB-PPy-PSS hybrid material. In the presence of PSS, pyrrole was polymerized by $Li_3Fe(CN)_6$. The presence of PPy and PSS served as a capping agent for the growth of cubic LiPB-PPy-PSS hybrids.

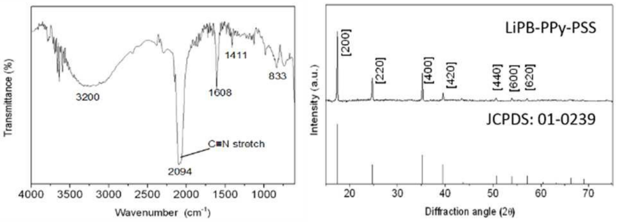

Fig. 2 FTIR spectrum (left) and XRD pattern (right) of LiPB-PPy-PSS hybrid.

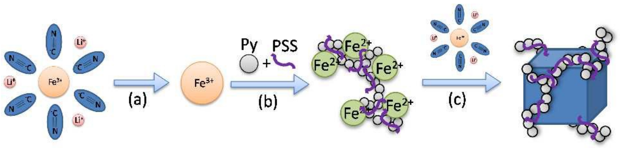

Fig. 3 Proposed schematic for the formation of LiPB-PPy-PSS hybrid. (a-b) Reduction of Fe^{3+} to Fe^{2+} and oxidation of Py monomers, and (c) formation of LiPB-PPy-PSS hybrid.

The cyclic voltammogram (Fig. 4(a)) and charge-discharge profile (Fig. 4(b)) showed that the LiPB-PPy-PSS hybrid has two operating voltage windows (discharge voltage or charging voltage) at 2.8–3.3 V and 3.8–4.4 V. The S-shaped potential profile indicated a solid solution reaction proceeding by intercalation, which was consistent with previous reports on PB analogs.[7] The appearance of a double shoulder (Fig. 4(b)) flattened out the charge-discharge curve of the LiPB-PPy-PSS hybrid, and was likely due to the presence of PSS doped-PPy in the hybrid material.[21] The p-doping effect of surfactant anions such as PSS on conductive polymers increased the conductivity of the hybrid, and could contribute to an increase in discharge capacity. A discharge capacity of ~ 120 mAh/g at a charging rate of 20 mA/g was achieved upon discharge. In contrast, the reported potassium PB-analog batteries showed a much lower initial discharge capacity, mostly < 70 mAh/g at a relatively low potential of < 1 V with respect to the standard hydrogen electrode.[7, 9]

In addition, our hybrid has a much better cyclability than previously reported $Fe_4[Fe(CN)_6]_3$ in Li-ion batteries.[14] Other analogs of PB, such as nickel and copper hexacyanoferrates were also similarly reported[12] to have severe capacity loss during cycling with Li$^+$. During galvanostatic cycling (Fig. 4(c)) between 1.5 V and 4.4 V at a charging rate of 20 mA/g, the discharge capacity of the pure Li-PB cathode decreased by > 50% after 10 cycles. The reason for the poor cyclability was due to the large Stokes radius of aqueous Li$^+$ of ~ 2.4 Å ,[12, 24] which led to destruction of the PB structure when the Li$^+$ ions moved through windows in the interstitial space of the PB crystal structure. The LiPB-PPy-PSS hybrid, however, demonstrated excellent electrochemical stability, retaining near 99% capacity after 10 cycles. After cycling for more than 200 cycles (Fig. 4(d)), the LiPB-PPy-PSS hybrid cathode retained > 80% of the initial discharge capacity, corresponding to a 0.09% drop per charge-discharge cycle. The slow fade of the discharge capacity could

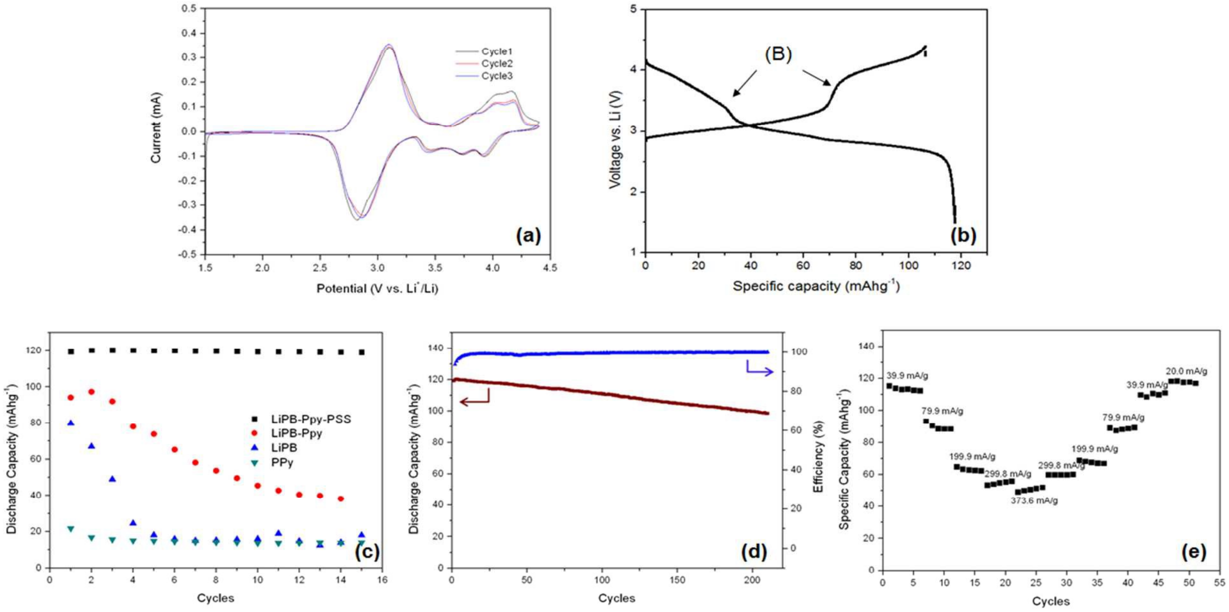

Fig. 4 (a) Cyclic voltammogram, (b) first charge-discharge curve with 'shoulders' (denoted by (B)), and (c–e) cycle performance of Li-PPy-PSS hybrid

partly attribute to the degradation of the metallic lithium anode due to the growth of dendrites or lithium fatigue during charge/discharge cycles.[23] The hybrid was also found to have excellent Coulombic efficiency of > 99.5% over the 200 charge-discharge cycles. The rate performance of the hybrid cathode was further tested at various charge/discharge currents (see Fig. 4(e)). The hybrid was first cycled at a constant current of 39.9 mA/g, and then cycled at various currents ranging from 20.0 mA/g to 373.6 mA/g. The results demonstrated that the hybrid has good rate capability across a wide range of discharge rates. This suggested that the polymeric matrix was able to buffer lattice strain effects during Li^+ insertion/extraction, resulting in an enhanced cyclability for the LiPB hybrid cathode. However, for the LiPB-PPy synthesized without PSS, although the cycling stability was much better than that of the pure LiPB cathode, a drop of > 5% discharge capacity per charge-discharge cycle was observed. The importance of PSS as an oxidizing agent, a charge compensator, and a template for polymerization has been previously reported for PSS-doped conductive polymers.[19] Due to the presence of free charges in the long strands of PSS, PPy doped with PSS has also been found to have a more hydrophilic surface and could maintain conductivity for longer periods, potentially improving charge-discharge performance.[18] To test the generality of this approach for the synthesis of other hybrids of hexacyanoferrate/conductive polymers, other monomers, such as 3,4-ethylenedioxythiophene (EDOT) and thiophene (Thio), were used to synthesize LiPB hybrids. The SEM images and charge/discharge performance of the LiPB-EDOT-PSS and LiPB-Thio-PSS hybrids are shown in Figs. S3 and S4, respectively, in the supporting information. The LiPB-EDOT-PSS and LiPB-Thio-PSS hybrids have stable discharge capacities of 102 mAh/g and 80 mAh/g, respectively, over 20 cycles, and have similar multifaceted cubic structures, demonstrating the facile nature of our synthesis method. It is important to recognize that this novel approach can potentially be extended to synthesize other MOFs via similar redox-coupled reactions. The formation of such MOF-conductive polymer hybrids can help to overcome the known insulating nature of many MOFs,[2] which may have precluded their use in electrochemical applications.

In summary, the synthesis of PB-conductive polymer hybrids via our one-pot redox chemistry approach takes place at relatively mild conditions in aqueous media, allowing for ease of scalability. The incorporation of conductive polymers significantly improves the cyclability and discharge performance of PB in Li-ion batteries. This synthetic strategy can potentially be extended to form other MOF-conductive polymer hybrids in a rapid and efficient manner.

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Notes and References

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