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A hyperbranched conjugated Schiff base polymer network: a potential negative electrode for flexible thin film batteries†

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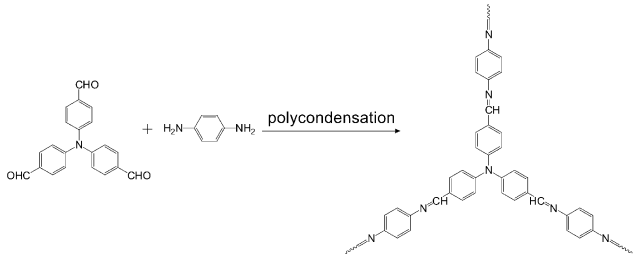
A hyperbranched conjugated Schiff base polymer network was synthesized by condensation between 4,4′,4″-nitrilotribenzaldehyde and *p*-phenylenediamine. The material exhibits excellent rate capability and long cycle life for lithium storage. Coupled with lower electrode potential (0.7 V *vs.* Li^+/Li), it may be well suited for fully flexible thin film polymeric batteries as the negative electrode.

The emerging market of wearable electronics presents an increasing demand for flexible thin film batteries, which has stimulated renewed interest in new electrode and electrolyte materials and new battery structures to fulfil the requirement for higher energy density, longer device lifespan and faster charging rate. The required flexibility represents a significant technical challenge because the physical connection among the inorganic particles, carbon supports and current collectors in the electrode coating deteriorates upon bending and thus degrades the battery performance. Redox polymeric substances combine the advantage of the intrinsic stretchability of polymers and the electrochemical activity of the redox sites, such as carboxyl,[1–3] quinone,[4–9] nitroxide radicals,[10–13] conjugated aromatics,[14,15] organosulfur[16] and polyaromatic amine.[17] Therefore, these materials may be suited as electrodes for flexible thin film batteries. Furthermore, organic polymeric electrode materials are potentially more cost effective and more environmentally sustainable because they can be derived from renewable resources.[18] Therefore, secondary batteries made largely of polymeric materials with high energy density are well suited for flexible electronic applications.

Unfortunately, the electrode potentials of the majority of organic electrodes reported to date lie between 2.5 and 4.0 V (*vs.* Li^+/Li). A pair of electrode materials for the construction of a full polymeric secondary battery with a cell voltage higher than 2.0 V has not yet been discovered.[19–21] Indeed, design of an organic electrode material with a substantially lower electrode potential is the key to the development of high-voltage fully polymeric secondary batteries.

Recently, a Schiff base (–CH=N–) was reported to exhibit a relatively low electrode potential from 0 to 1.5 V (*vs.* Na^+/Na) for sodium storage.[22] The work inspired us to speculate that the Schiff base might be an appropriate organo functional group to be used in a redox polymeric anode. With the idea in mind, we designed and synthesized a hyperbranched conjugated Schiff base polymer through polycondensation between 4,4′,4″-nitrilotribenzaldehyde and *p*-phenylenediamine. The reaction scheme is shown in Scheme 1. The π conjugation in the precursor molecules is substantially enhanced upon polymerization, which subsequently gives rise to strong structural stability. Detailed information on the synthesis and characterization can be found in the ESI.†

The synthesized hyperbranched conjugated Schiff base polymer is a bright orange powder. The morphology characterized by FE-SEM is shown in Fig. 1(a), which reveals significant agglomeration of irregular shaped particles. The FTIR spectra of the reactants and the product are depicted in Fig. 2(b). For *p*-phenylenediamine, 3409 cm^{-1} ($\nu_{N\text{–}H}$, as, $-NH_2$), 3372 cm^{-1} ($\nu_{N\text{–}H}$, s, $-NH_2$), 1632 cm^{-1} ($\delta_{N\text{–}H}$, $-NH_2$), 1261 cm^{-1} ($\nu_{C\text{–}N}$, $Ar\text{–}NH_2$), 832 cm^{-1} ($\delta_{Ar\text{–}H}$, 1,4-substitued benzene), and 717 cm^{-1} ($\gamma_{N\text{–}H}$, $-NH_2$). For 4,4′,4″-nitrilotribenzaldehyde, 2832 cm^{-1} ($\nu_{C\text{–}H}$, –CHO), 2734 cm^{-1} ($\delta_{C\text{–}H}$, –CHO), 1688 cm^{-1} ($\nu_{C=O}$, –CHO), 1275 cm^{-1} ($\nu_{C\text{–}N}$, $Ar\text{–}NH_2$), and 816 cm^{-1} ($\delta_{Ar\text{–}H}$, 1,4-substitued benzene). For the hyperbranched conjugated Schiff base polymer, 1688 cm^{-1} and 1619 cm^{-1}



Scheme 1 Synthesis of a conjugated Schiff base polymer.

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† Electronic supplementary information (ESI) available: Detailed information on 4,4′,4″-nitrilotribenzaldehyde & polymer synthesis, characterization, battery assembly and bending test. See DOI: 10.1039/c5cc09662f

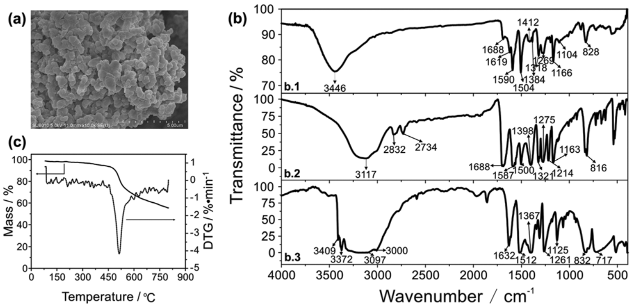

Fig. 1 (a) FE-SEM image; (b) FTIR spectra: (b.1) conjugated Schiff base polymer, (b.2) 4,4′,4″-nitrilotribenzaldehyde, (b.3) *p*-phenylenediamine; (c) TGA analysis.

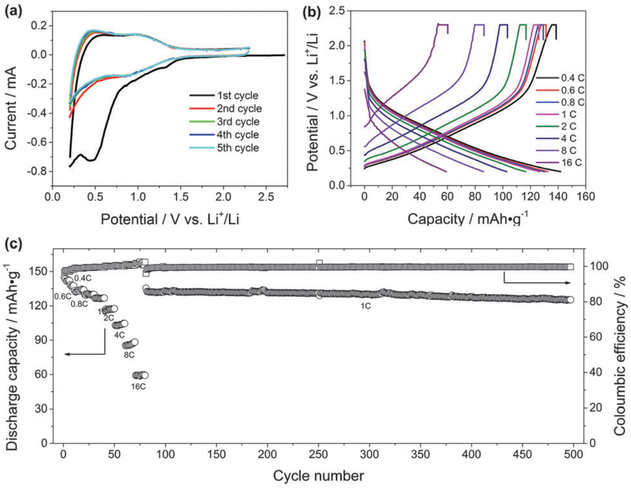

Fig. 2 Electrochemical measurement of the conjugated Schiff base polymer in a half cell. (a) Cyclic voltammetry; (b) charge and discharge plateaus at different C-rates; and (c) rate capability and cycle performance.

($\nu_{C=N}$, Ar–CH=N–Ar), 1269 cm^{-1} (ν_{C-N}, Ar–CH=N–Ar), and 823 cm^{-1} (δ_{Ar-H}, 1,4-substitued benzene). Upon the polycondensation, the characteristic absorption peaks of the aromatic amine as well as the aldehyde disappeared, indicating a rather complete reaction of the cross condensation. The thermal gravimetric analysis is shown in Fig. 1(c) indicating that the conjugated Schiff base polymer maintains roughly 95 wt% up to 400 °C and a significant weight loss occurs at around 460 °C. The results reflect the strong thermal stability of the material.

Cyclic voltammetry was performed with a half cell using a lithium metal foil as the counter electrode as well as the reference electrode (Fig. 2(a)). The open circuit potential of the half cell was found to be 2.7 V (*vs.* Li$^+$/Li) corresponding to the oxidation state of the hyperbranched conjugated Schiff base polymer. The electrode was scanned from the open circuit potential to 0.2 V and then reverse-scanned to 2.3 V, recording fifteen cycles. In the first cycle, there is an irreversible electrochemical reduction current peak, which is ascribed to the formation of a solid electrolyte interfacial (SEI) film and/or reduction of organic residues. In the subsequent four cycles, the *I–V* curves vary only modestly. Another ten cycle curves also almost overlap, which can be found in the ESI.† Notably, there are two current peaks between 0.2 V and 1.5 V, corresponding to the electrochemical oxidation and reduction processes of the Schiff base. Above 1.5 V, it is a non-Faradic process. Furthermore, both the oxidation and the reduction current curves are nearly symmetric, indicating that the electrochemical processes with the hyperbranched conjugated Schiff base polymer are highly reversible. The reversibility is further evidenced from the rate and cycle performance as shown in Fig. 2(b) and (c). From the galvanostatic charge and discharge curves at 0.4C in Fig. 2(b), we estimate that the reversible electrode potential for the conjugated Schiff base polymer electrode is around 0.7 V (*vs.* Li$^+$/Li) and its reversible capacity is approximately 140 mA h g^{-1}. Indeed, the half cell was found to deliver 140 mA h g^{-1} at 0.4C, 129 mA h g^{-1} at 0.8C, 127 mA h g^{-1} at 1C, 118 mA h g^{-1} at 2C, 104 mA h g^{-1} at 4C, 86 mA h g^{-1} at 8C and 60 mA h g^{-1} at 16C. The discharge capacity remains nearly a half of the initial capacity value at 16.0C, exhibiting excellent reversibility. Subsequently, the half cell was charged and discharged for additional 400 cycles at 1C. The discharge capacity declines only marginally and the coulombic efficiency remains above 99%, exhibiting outstanding electrochemical stability.

The redox reactions occur in the polymer matrix with the functional groups exposed to the liquid electrolyte, which enables lithium ions to diffuse readily throughout the polymer network. The process is still Faradic. Indeed, the Schiff base functional groups are reduced to radical anions by accepting electrons from lithium upon discharge and, in the reverse process, the radical anions are oxidized to the Schiff base by losing electrons upon charge. Structurally, the polymer matrix differs significantly from the conventional crystalline based inorganic electrode materials where redox reaction takes place *via* lithium insertion/desertion. Furthermore, the oxidation and reduction current curves are essentially symmetric (Fig. 2(a)). As a result, the π conjugated Schiff base polymer undergoes rapid charge/discharge without a significant loss of discharge capacity.

A flexible battery is required to resist stretching and bending. To test the mechanical properties of the electrode film, we prepared a pouch cell and conducted a series of tests on the tensile strength of the hyperbranched Schiff base polymer and the electrochemical properties of the cell upon bending with careful characterization. The measurement details are presented in the ESI.† The tensile strength and the elongation rate of the electrode film were found to be 0.28 MPa and 13%, respectively, in a dry state. The EIS data were collected at various bending radii and bending degrees as shown in Fig. 3. Clearly, the charge transfer resistances change only marginally in comparison with the unbent state. The results indicate that the hyperbranched conjugated Schiff base electrode film is capable of accommodating mechanical bending.

In conclusion, a hyperbranched conjugated poly(4,4′,4″-nitrilotribenzaldehyde-*co*-*p*-phenylenediamine) Schiff base polymer was successfully synthesized and well characterized. Due to the high degree of π conjugation, the hyperbranched conjugated Schiff base polymer exhibits outstanding electrochemical reversibility and stability for lithium storage. In addition, the hyperbranched network is benefit for structural integrity and electrochemical stability as verified by the bending measurements on the fabricated

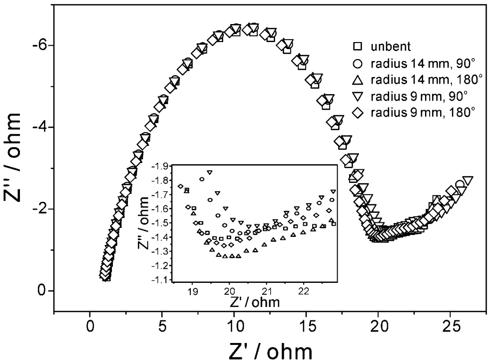

Fig. 3 EIS measurement on a pouch cell at different bending radii (9 mm and 14 mm) and bending degrees (90° and 180°) with the polymer electrode facing outwards. Enlarged view at the corner is inserted.

pouch cell. Coupled with its lower electrode potential (0.7 V *vs.* Li^+/Li), the material may be well suited for fully flexible thin film polymeric batteries as the negative electrode.

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