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## High power organic cathodes using thin films of electropolymerized benzidine polymers†

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Thin films of benzidine polymers were electrochemically deposited directly onto conductive substrates by oxidative coupling of di- and trianilinoalkane monomers. The electropolymerization and electrochemical properties of the polymers were optimized by varying the alkyl linker. Polymer films exhibited two reversible one-electron transfers at high potentials (>3.3 V vs. Li/Li<sup>+</sup>) and maintained discharge capacities in excess of 150 mA h g<sup>-1</sup> even when discharged in under 4 seconds.

The demand for and integration of sustainable energy technologies and the intermittent nature of renewable energy sources, such as solar and wind, promotes the advancement of electrochemical energy storage (EES) systems.<sup>1</sup> Lithium ion batteries (LIBs) are employed in a wide range of applications, from portable electronics and electric vehicles to grid energy storage, due to their high energy and power densities. However, current LIBs do not meet the performance requirements for future applications, especially automotive and grid applications.<sup>2</sup> The disparity between conventional cathodes (e.g. LiCoO2, LiFePO4) and anodes (e.g. LiC<sub>6</sub>) in terms of capacity, cost and abundance, motivates research on alternative cathode materials such as organic compounds.<sup>1a,3</sup> Organic molecules are especially attractive for EES applications because they can be designed and tuned to be light weight and capable of multiple electron transfers at high potentials, thereby maximizing gravimetric capacity and energy density to potentially achieve values greater than commercial LIBs (>160 mA h  $g^{-1}$ > 250 W h kg<sup>-1</sup>), although at lower volumetric energy densities.<sup>4</sup>

In the field of organic electrodes, thin electroactive polymer films have attracted interest as electrodes in flexible batteries for wearable technologies and microbatteries for miniaturized electronic devices.<sup>5</sup> Thin films of redox-active amorphous polymers are mechanically flexible and can have high power densities because of the short ion transport lengths and the fact that (dis)charge processes do not

batteries. The conductivity and insolubility of conducting polymers are attractive features but the small capacities, due to low doping levels and sloping charge/discharge curves, limit their usefulness.<sup>5a</sup> Nitroxide-based polymers are stable for hundreds of cycles, but they typically undergo only one electron transfer per repeat unit, and consequently, have limited specific capacity.9 The practical use of organic materials requires the development of electrodes with better performance. We have been involved in the design (in silico), synthesis and characterization of organic based cathode materials for EES applications.<sup>10</sup> We are especially interested in materials that can not only exchange multiple electrons per formula unit at high potentials, but that can also sustain high charge and discharge rates. Such a system would combine the energy density of a battery with the power density of a supercapacitor. Furthermore if such a material could be generated via electropolymerization, thus yielding a conformal film on any conductive substrate serving as current collector, one could have a system with an arbitrary "form factor." Herein we describe an electropolymerized benzidine polymer that can be reversibly oxidized in two one-electron steps at high potentials  $(>3.3 \text{ V vs. Li/Li}^{+})$  and at fast rates (1000 C), with minimal capacity loss after one hundred cycles. In other words, we have developed a cathode material with the voltage plateaus and high capacities characteristic of batteries, but capable of the high cycling rates of supercapacitors.

involve intercalation.<sup>5b,6</sup> Conducting polymers (e.g. polypyrrole)<sup>7</sup> and

radical polymers<sup>8</sup> have been employed as cathodes in paper-based

We were interested in investigating N,N,N',N'-tetramethylbenzidine (TMB) as a potential cathode material because of its two reversible oxidations to the quinoidal dication at high potentials (>3.3 V vs. Li/Li<sup>+</sup>).<sup>11</sup> However, the solubility of small molecules precludes their feasibility as electrode materials. Our strategy to overcome those issues was to incorporate TMB moieties into insoluble polymers through the oxidative coupling of anilines (Scheme 1). For example, TMB is the well-known coupling product of the oxidation of N,N-dimethylaniline (DMA).<sup>12</sup> Other groups have exploited this coupling to form benzidine polymers using monomers with at least two aniline groups.<sup>13</sup> We studied the electropolymerization and electrochemical properties of benzidine

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Scheme 1 Electropolymerization of DA-n monomers and the oxidation of PDA-n.

films with varying alkyl linkers between the polymerizable end groups to develop a redox-active polymer with excellent cycling stability and high capacities at fast rates.

A series of di- and trianilinoalkanes was synthesized with different alkyl lengths connecting the anilines (Fig. 1a). Based on the oxidation of DMA, these monomers should electropolymerize to form polymer films on the electrodes. Electropolymerization is a valuable technique to deposit conformal films directly on conductive surfaces. Moreover, film thickness and morphology can be controlled.<sup>14</sup> Scheme 1 shows the proposed mechanism for the electropolymerization of DMA to TMB.<sup>12</sup> Initially, the dianiline (**DA-n**) oxidizes to the radical cation that can form a C–C bond at the *para*position of the anilines with another **DA-n<sup>+•</sup>**. Deprotonation affords the neutral dimer that can continue the process of oxidation, coupling, and deprotonation. At sufficient molecular weight,



Fig. 1 (a) Cyclic voltammograms (CV) of 10 mM monomer in 0.1 M [(<sup>n</sup>Bu)<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> on the 1st (–) and 2nd cycle (–). (b) CVs of electrodes prepared from (a) cycled in 0.1 M [(<sup>n</sup>Bu)<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>3</sub>CN. All CVs on 100  $\mu$ A scale except as indicated. Scan rate: 20 mV s<sup>-1</sup>.

the polymer precipitates and deposits on the electrode. Oxidation of benzidine in the repeat unit of the polymer (**PDA-n**) forms the radical cation (**PDA-n**<sup>+•</sup>) that can be further oxidized to the quinoidal dication, **PDA-n**<sup>2+</sup> (Scheme 1). The benzidine polymers have theoretical capacities of 170–224 mA h g<sup>-1</sup>, which are greater than the practical capacity of LiCoO<sub>2</sub> (140 mA h g<sup>-1</sup>).

Fig. 1a shows the cyclic voltammograms (CV) of 10 mM monomer in 0.1 M [( $^{n}$ Bu)<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> at glassy carbon electrodes (GCE). On the first cycle (—), all of the monomers begin oxidizing at >+0.42 V vs. Ag/Ag<sup>+</sup>. The appearance of two reduction peaks on the subsequent negative sweep corresponds to the newly formed benzidine, indicating that the oxidative coupling was successful. These assignments were based on similar observations in the coupling of DMA to TMB.<sup>12</sup> **DA-2** and **TA-2** were the only monomers that did not display two reduction peaks suggesting unwanted side reactions. On the second cycle (—), some of the monomers display a new oxidation peak between 0–0.2 V that also corresponds to benzidine. The increase in reduction peak currents on successive cycles is indicative of polymer deposition and film growth.

After electropolymerization, the electrodes were rinsed with CH<sub>2</sub>Cl<sub>2</sub> to remove soluble oligomers and cycled in monomer-free 0.1 M  $[(^{n}Bu)_{4}N]$  [PF<sub>6</sub>] in CH<sub>3</sub>CN (Fig. 1b). As expected from Fig. 1a, there was no Faradaic (redox) response for electrodes cycled in DA-2 or TA-2. All of the other modified electrodes exhibited two redox couples, corresponding to the PD(T)A-n/PD(T)A-n<sup>+</sup> and the PD(T)A-n<sup>+</sup>/PD(T)A-n<sup>2+</sup> couples, referred to in this report as the first and second redox couples, respectively. As the alkyl linker size was increased from C2 to C4, the Faradaic response of the modified electrodes also increased which indicates that more polymer was deposited onto the electrode. This trend suggests that there are repulsive interactions between charged benzidine moieties that interfere with the electropolymerization and film deposition process. Alkyl linker size also has an effect on the electrochemistry of the polymer films. The first redox couples of PDA-3 and PDA-4 have a large peak to peak separation  $(\Delta E_{\rm p} > +0.19 \text{ V})$  while **PDA-6** and **PTA-6** have  $\Delta E_{\rm p} < +0.09 \text{ V}$ . The  $\Delta E_{\rm p}$  is expected to be 0 V for kinetically facile surface-confined systems and the non-zero  $\Delta E_{\rm p}$  for the polymer films can be partially accounted for by the fast scan rate, since at slower scan rates, the  $\Delta E_{\rm p}$ s of **PDA-6** approached 0 V (Fig. S2, ESI<sup>†</sup>). The second redox couple for all films had  $\Delta E_{\rm p}$  < +0.09 V and the oxidation potentials shift negative with increasing alkyl linker length in the transition from PDA-n<sup>+</sup>• to PDA-n<sup>2+</sup>. This negative shift indicates that the dication is more stable (*i.e.* it is easier to oxidize the radical cation) with longer alkyl chains between the charged benzidine moieties.

Along with the linker size of the monomers, we studied the effect of solvent polarity on the electropolymerization of **DA-6** (Fig. S3, ESI<sup>†</sup>). The onset of monomer oxidation shifts negative in more polar solvents, *e.g.* from +0.41 V in  $CH_2Cl_2$  to 0.25 V in  $CH_3CN$ . The cathodic peak currents are larger in lower dielectric solvents and correspondingly, more polymer was deposited on the electrodes. Dichloromethane was found to be the best solvent for the electropolymerization, and a higher concentration of electrolyte (0.5 M) was used to lower the solution resistance.

The progress of **DA-6** electropolymerization and the charged state of **PDA-6** can be followed visually due to the electrochromic properties of benzidines (Movies, ESI<sup>†</sup>). The indium tin oxide (ITO)



Fig. 2 (a) Contour plot of the *in situ* UV-vis spectroelectrochemistry of **PDA-6** deposited onto ITO electrode during one cycle. Inset: Corresponding CV of **PDA-6** film cycled in 0.1 M [ $(^{n}Bu)_{4}N$ ][PF<sub>6</sub>] in CH<sub>3</sub>CN at 10 mV s<sup>-1</sup> with Roman numeral markers relating designated potentials to UV-vis spectra. UV-vis spectra of **PDA-6** at designated potentials (b) between -0.10-0.22 V for the **PDA-6/PDA-6<sup>++</sup>** couple and (c) between +0.20-0.60 V for the **PDA-6<sup>++</sup>**/**PDA-6<sup>2+</sup>** couple. (d) Pictures of **PDA-6** film on ITO in the neutral, cationic and dicationic states.

electrode is colorless at potentials before the first redox couple, turns green during the first redox couple, and marigold during the second redox couple. The changes in absorbance of PDA-6 deposited on ITO were monitored throughout one cycle by in situ spectroelectrochemistry. The contour plot of UV-vis spectra (Fig. 2a) demonstrates that the spectroelectrochemistry of PDA-6 is highly reversible and symmetric. The UV-vis spectra of the ITO electrode at potentials during the first redox couple contain several well-defined isosbestic points at 360, 498, and 565 nm (Fig. 2b), while the UV-vis spectra of the second redox couple contain two isosbestic points at 411 and 570 nm (Fig. 2c). The isosbestic points indicate that the polymer cleanly and reversibly converts between the three redox states. The spectra of neutral PDA-6 at potentials I and IX, before any oxidation and after complete reduction respectively, overlap entirely. Similarly, the spectra match at potentials III and VII when the polymer has been oxidized and reduced to PDA-6<sup>+•</sup> respectively. The electrochromic nature of PDA-6 means the state of charge can be determined visually in transparent EES devices, and the films displayed typical switching times for electrochromic polymer films on the order of 1–2 seconds (Fig. S9 and S10, ESI<sup>†</sup>).<sup>15</sup>

The applicability of this family of benzidine polymers, as cathode materials in thin-film electrochemical energy storage systems, was initially examined by cycling the electropolymerized films using CV in 0.1 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>3</sub>CN. Further studies focused on **PDA-6** because the polymer, with a theoretical capacity of 181 mA h g<sup>-1</sup>, exhibits two well-behaved redox couples and great charge retention (Fig. S5, ESI<sup>†</sup>). Cycle-life performance testing was conducted using galvanostatic cycling experiments at different current densities. Thin films of **PDA-6** were electrodeposited onto GCE in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> and cycled in 0.5 M [( $^{n}Bu$ )<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub>

The discharge curves in Fig. 3a display two voltage plateaus at approximately +0.31 and 0 V vs. Ag/Ag<sup>+</sup> (3.6 and 3.3 V vs. Li/Li<sup>+</sup>) that correspond closely to the two reductions from PDA-6<sup>2+</sup> to neutral PDA-6. Remarkably, at rates of 100-1000 C, the thin film was discharged to  $\sim 165$  mA h g<sup>-1</sup> (or 5.09 mC cm<sup>-2</sup>). At the charge rate of 1000 C, the polymer was fully discharged in less than 4 s. The higher current densities at high C rates lead to an increase in the IR voltage drop due to the internal cell resistance, lowering cell performance. Contrary to most systems, including 50 nm polymer films,<sup>7a,9c</sup> the capacity did not decrease considerably at high current rates for PDA-6. While the discharge plateaus shifted negative at faster rates, as expected, the IR drop was not significant, even at 1000 C, to dramatically impact the capacity (only a 2% decrease in capacity with a tenfold increase in rate). The remarkable rate capability of PDA-6 is a result of the rapid kinetics of the two electron transfer reactions ( $k_s = 0.4, 0.5 \text{ s}^{-1}$ ) and the efficient charge propagation within the 100 nm polymer film, which has diffusion coefficients on the order of  $10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> (Fig. S6 and S7, ESI†).

The comparable capacities at high C rates prompted additional tests of thin films of PDA-6 as a high power cathode material. Fig. 3b shows the cycling performance of the PDA-6 film charged and discharged at 1000 C for 100 cycles at two different positive potential limits. If the polymer was only cycled between the PDA-6/PDA-6\*• couple in the range -0.1-0.2 V vs. Ag/Ag<sup>+</sup>, the capacity is 74 mA h g<sup>-1</sup> and the film displays excellent cycle performance with >99% discharge retention after 100 cycles and > 96% Coulombic efficiency. When the range was expanded to -0.1-0.5 V, PDA-6<sup>+•</sup> can be further oxidized to PDA- $6^{2+}$ , thereby increasing the capacity to 165 mA h  $g^{-1}$ . We accessed 91% of the theoretical capacity of 181 mA h  $g^{-1}$  in the thin film. The polymer film exhibited good cycling stability with 92% discharge retention after 100 cycles and >98% Coulombic efficiency. Similar trends were seen in PDA-6 films cycled at slower rates (Fig. S11, ESI<sup>+</sup>). Using capacity values of 74 and 91 mA h g<sup>-1</sup> for the first and second redox processes, respectively, at voltages of



Fig. 3 (a) Discharge curves for **PDA-6** at various C rates. (b) The capacity (red) and Coulombic efficiency (blue) of **PDA-6** with different positive cutoffs in 0.5 M [(<sup>n</sup>Bu)<sub>4</sub>N][PF<sub>6</sub>]/CH<sub>3</sub>CN at rate of 1000 C. Inset: Representative charge and discharge curves for **PDA-6** with different potential ranges. The range was -0.1-0.2 V (square) and -0.1-0.5 V (triangle) vs. Ag/Ag<sup>+</sup>.

3.3 and 3.6 V vs. Li/Li<sup>+</sup>, we obtain energy densities of 244 and 327 W h kg<sup>-1</sup>. Moreover, at a C rate of 1000, and using the abovementioned energy densities, they represent very high power densities of 2.4 and  $3.3 \times 10^5$  W kg<sup>-1</sup>.

When the polymer film was cycled around both redox couples, the total capacity was expected to have equal contribution from each redox couple. However, the second redox couple had a higher capacity than the first (91 compared to 74 mA h  $g^{-1}$ ). The additional capacity can be accounted for by the flatter discharge plateau at +0.31 V than at 0 V which enables more capacity from the PDA-6<sup>+•</sup>/PDA-6<sup>2+</sup> couple than the PDA-6/PDA-6<sup>+•</sup> couple (Fig. 3a). Also, the charge calculated from a CV of PDA-6 film reveals that there is more charge from the second redox couple than the first couple (Fig. S8, ESI<sup>+</sup>). One possible reason for this imbalance is that the film contains fragments of PDA-6<sup>+</sup> that can be oxidized to PDA-6<sup>2+</sup> but not reduced to PDA-6. This charge trapping phenomenon was also seen in films of PTA-6 where the capacity of the first redox couple decreases relative to the second couple during cycling (Fig. S12, ESI<sup>†</sup>). Attempts to improve charge retention by co-electropolymerizing the crosslinker TA-6 with DA-6 also gave rise to charge trapping and poorer cycling than PDA-6.

In summary, we have developed a series of di- and trianilinoalkanes capable of forming thin electroactive films directly on electrodes, by electrochemical oxidative polymerization. Increasing the length of the alkyl linker between aniline groups facilitated the electropolymerization process and more polymer was deposited on the electrode. In comparison to shorter alkyl analogs, PDA-6 and PTA-6 exhibit two redox couples with small  $\Delta E_{\rm p}$ s. PDA-6 displays reversible electrochromic behavior as the neutral, colorless polymer turns green as the radical cation (PDA- $6^{+\bullet}$ ) and marigold as the dication (PDA- $6^{2+}$ ) are generated. The ability to visually identify the state of charge of the cathode material could be useful in transparent EES devices. Due to the fast kinetics of the two electron transfers and the 100 nm thick film. PDA-6 can be charged and discharged at rates up to 1000 C without an appreciable loss in capacity. The polymer displayed exceptional stability (>99% retention) when cycled only around the first couple. When the polymer is fully oxidized to PDA-6<sup>2+</sup>, there are two distinct voltage plateaus and the film retains 92% of the initial capacity of 165 mA h  $g^{-1}$  after 100 cycles. These findings indicate the potential usage of PDA-6 as a cathode material in thin-film batteries that combines the high capacity of batteries with the high power of supercapacitors. Investigation is currently underway to use the polymers on high surface area electrodes for 3D and flexible batteries.

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