ACS APPLIED MATERIALS & INTERFACES

# Viologens as Charge Carriers in a Polymer-Based Battery Anode

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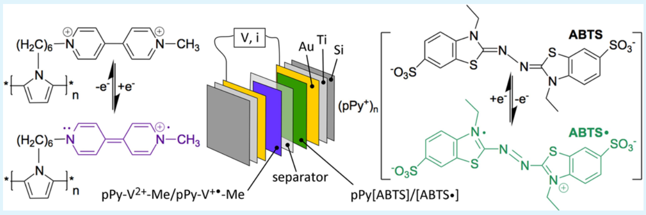
**ABSTRACT:** Viologens, either as anions in solution or as pendant substituents to pyrrole, were incorporated as dopants to electrodeposited films of polypyrrole. The resulting polymer films exhibited redox activity at −0.5 V vs Ag/AgCl. The film consisting of polypyrrole with pendant viologens exhibited the best charge−discharge behavior with a maximum capacity of 55 mAh/g at a discharge current of 0.25 mA/cm$^2$. An anode consisting of polypyrrole (pPy) doped with viologen (V) was coupled to a cathode consisting of pPy doped with 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) to yield a polymer-based battery with a cell electromotive force (emf) of 1.0 V, maximum capacity of 16 mAh/g, and energy density of 15 Wh/kg.



**KEYWORDS:** *polymer batteries, conducting polymers, viologens, redox-active dopant*

## 1. INTRODUCTION

Several approaches to low-cost, flexible batteries and supercapacitors have been demonstrated, including the use of carbon nanotubes,[1−5] conducting polymers (CPs),[6−15] nonconjugated radical polymers,[16−18] or some combination thereof.[19−22] In a series of papers by Nishide et al.,[16,23−29] one of the more promising approaches to organic batteries has been reported where nitroxide-radical-based polymers were used as anode and cathode materials. Both *p*-type and *n*-type redox polymers were synthesized by carefully controlling the electronic effects of substituents to yield a battery consisting of only organic materials. This battery was shown to exhibit half-cell capacities up to 80 mAh/g. The battery demonstrated excellent rate capability, because of the fast electron transfer kinetics of nitroxyl radicals.[29] Crispin et al. reported an all-polymer battery with an electromotive force (emf) of 0.5 V, using an anode and cathode based on poly(3,4-ethylenedioxythiophene) (PEDOT).[30] The presence of polyethyleneimine ensures a low oxidation state of the PEDOT anode, promoting its stability in air. Wallace et al.[31] reported the use of functionalized polyterthiophenes as an anode, which was coupled to a pPy cathode to achieve capacities up to 95 mAh/g. A considerable loss in capacity (50%) was observed after 150 cycles of repeated charging and discharging, which was attributed primarily to mechanical degradation of the polymer. Several composites consisting of conducting polymers (CPs) and carbon nanotubes (CNTs) have been reported as battery materials, although most are targeted for use in supercapacitors.[3,4,32−34] The use of microstructured or nanostructured cellulose in these CP/CNT-based composites also has been studied because of the low cost, abundance, and flexibility of a cellulose matrix.[19,35−37] Nystrom et al.[38] reported a battery based on a cellulose−polypyrrole (cellulose-pPy) composite exhibiting capacities up to 50 mAh/g with only a 6% loss of capacity after 100 cycles of charging and discharging. In addition, this battery could be operated at current densities up to 600 mA/cm$^2$.

In this paper, we report on the charge-carrying capacity and stability of electrodeposited films of pPy doped with viologen constituents that are either electrostatically bound or covalently attached to the pyrrole monomer. Three different polymer films were studied and compared: (1) polypyrrole doped with 1,1′-bis(ethylsulfonate)-4,4′-bipyridinium dibromide (pPy-[VDS]), (2) polypyrrole doped with 1,1′-bis(2,4-benzenedisulfonate)-4,4′-bipyridinum dibromide (pPy[VTS]), and (3) polypyrrole with covalently attached viologen (pPy-V$^{2+}$-Me). These films are of interest because of their potential to improve the performance parameters of a battery based on conducting polymers doped with redox active molecules.[39] For example, a battery consisting of pPy doped with indigo carmine (pPy[IC]) as anode and pPy doped with 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) (pPy[ABTS]) as cathode exhibits a cell emf of 0.52 V. This voltage is due to the reversible redox potentials of IC and ABTS at 50 mV and 570 mV (vs Ag/AgCl), respectively.[40] To increase the cell emf of the battery, other redox-active dopants with more negative redox potentials that IC or more positive redox potentials than ABTS are needed.

Derivatives of 4,4′-bipyridine, commonly known as viologens, possess three, one-electron redox states (V$^0$, V$^{+\bullet}$, and V$^{2+}$) that exhibit rapid, reversible rates of electron transfer at potentials in the range of −0.4 V to −1.0 V vs Ag/AgCl.[41−43] Thus, incorporation of viologens into the anodic film of a battery will increase the cell emf of a battery to at least 1.0 V. Viologens have been used as redox mediators,[44,45] in molecular electronics[46] and electrochromics,[46−50] and other electrochemical applications.[51−53] Typical examples are benzyl and

**Received:** April 29, 2013
**Accepted:** July 23, 2013
**Published:** August 8, 2013

dx.doi.org/10.1021/am401590q | *ACS Appl. Mater. Interfaces* 2013, 5, 7825−7830

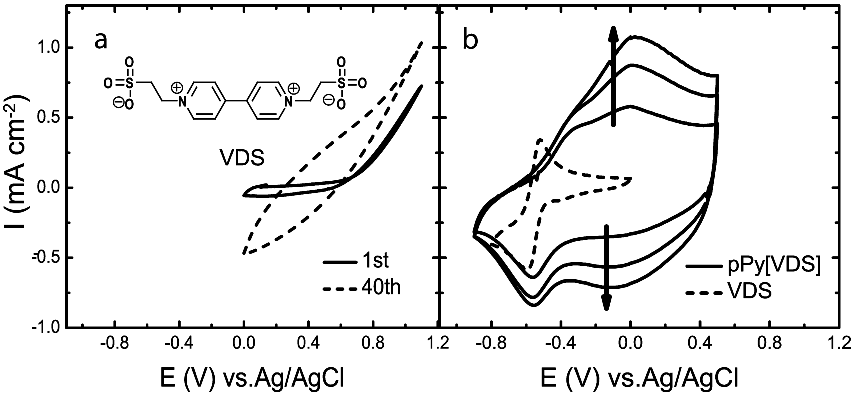


**Figure 1.** (a) Cyclic voltammograms obtained during the electropolymerization of 200 mM pyrrole in the presence of 25 mM VDS over 40 cycles at a scan rate of 100 mV/s (molecular structure of VDS shown in the inset); (b) cyclic voltammograms of a pPy[VDS]-coated Au electrode immersed in 0.2 M KCl at a scan rate of 100 mV/s equilibrated over 100 consecutive cycles; corresponding cyclic voltammogram of VDS in solution (2.5 mM VDS in 0.2 M KCl, dashed line) are shown at 100 mV/s.

methyl viologens, which exhibit reversible redox chemistry at −0.5 ($V^{2+}$ and $V^{+\bullet}$) and −0.9 V ($V^{+\bullet}$ and $V^0$). While these potentials are attractive for increasing the cell emf of a battery, ambient oxygen must be excluded to prevent deleterious reactions between reduced forms of viologen and oxygen.[41]

Several methods have been developed to immobilize viologens on electrodes including deposition of a chemically preformed polymer,[54−58] incorporating the viologen into a polymer matrix,[59−73] and electrochemical polymerization of a monomer with a covalently attached viologen.[60,67,69,74] Deposition of a chemically preformed polymer has been used for electrochromic devices where the viologen polymers are incorporated as a multilayer or in the form of a polymer complex with a polyanion such as poly(styrene sulfonate).[46] Such poly(alkyl viologens) form the basis of electrochromic windows, given their rapid change between a transparent state and a violet color.[28,46] This method of immobilization, however, often is limited because of solubility issues and the consequential inhomogeneous films deposited. Covalent linkage of viologen with a polymerizable monomer has certain advantages, with respect to solubility and versatility.[63,74] Viologens have been incorporated into films of CPs such as poly(3,4-ethylenedioxythiophene) (PEDOT) and pPy via covalent linkage to the polymer backbone.[74] These composite materials are of interest because they possess both redox conductivity from redox self-exchange and the intrinsic electronic conductivity of the CP. At the potential where viologens are redox active, however, the polypyrrole in a pPy-viologen film is essentially insulating and thus, redox self-exchange reactions dominate the electron transport properties of these films.[67,74,75] Previous reports of such CP-viologen composites focused exclusively on electrochromic applications. In this report, CP-viologen composites are studied for their suitability as anode materials in polymer-based batteries.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis.** All chemicals were purchased from Aldrich and used as received, unless specified otherwise. All chemical structures were confirmed by $^1$H NMR spectra recorded on a Bruker 300 MHz spectrometer. Mass spectra were collected on a Hewlett−Packard (Agilent) GCD 1800C GC-MS or on a Thermo LCQ_DECA XP Max-Ion trap MS with a Shimadzu HPLC system in negative ion mode (Neg-ESI-MS). Pyrrole was distilled prior to use and stored under argon. 1-methyl-1′-(6-pyrrol-1-yl)hexyl)-4, 4′-bipyridinum [Py-$V^{2+}$-Me] dichloride,[74] 4-(bromomethyl)-1,3-benzenedisulfonic acid disodium salt,[76] 1,1′-bis (ethylsulfonate)-4,4′-bipyridinium dibromide[77] were synthesized following previously described methods.

*Synthesis of 1,1′-bis(2,4-benzenedisulfonate)-4,4′-bipyridinum Dibromide.* A solution of 4, 4′-bipyridinium (0.312 g, 2 mmol) and sodium 4-(bromomethyl)-1,3-benzenedisulfonic acid, disodium salt (1.5 g, 4 mmol) was stirred in 20 mL dry DMSO at 90 °C for 20 h. After the solvent was removed under reduced pressure, the bipyridinium salt was recrystallized twice from ethanol−water (4/1 v/v) and dried under vacuum; (0.325 g, 19%). $^1$H NMR ($D_2O$): $\delta$ 9.38 (4H, d), 8.63 (4H, d), 8.16 (s, 2H), 7.62 (d, 2H), 7.49 (d, 2H), 6.25 (s, 4H); mass (Neg-ESI-MS): $m/z$ 654 ($M^+$).

**2.2. Electrochemistry.** A three-electrode system in a single compartment cell was used for electrochemical synthesis and characterization of the polymer films. The working electrode was a gold disk (0.2 cm$^2$), and the counter electrode was platinum mesh. The reference electrode was either Ag/AgCl when using an aqueous electrolyte or sodium saturated calomel electrode (SSCE) in combination with a salt bridge containing 0.2 M $LiClO_4$/acetonitrile (ACN) when using a nonaqueous electrolyte. An EG&G (Model 263A) potentiostat/galvanostat was used for all electrochemical experiments. The electrochemical cells were purged with $N_2$ for 15 min prior to each experiment and a $N_2$ blanket was maintained throughout all electrochemical measurements. A microbalance (AX21 comparator, Mettler−Toledo) was used to determine the weight of the electrodeposited films.

*Half-Cell Experiments.* Films of pPy-$V^{2+}$-Me were synthesized by potentiodynamic electropolymerization of a 10 mM solution of Py-$V^{2+}$-Me in 0.2 M $LiClO_4$/ACN. The potential of the working electrode was swept between 0 V and 1.5 V vs SSCE for 80 cycles at a scan rate of 100 mV/s. The resulting films of pPy-$V^{2+}$-Me were charged potentiostatically for 300 s at −0.85 V vs SSCE and subsequently discharged over a range of current densities (0.25 to 5 mA cm$^{-2}$). The discharge curves (potential vs time) provide information about the charge carrying capacity of these films as

$$(\text{capacity}) = (\text{discharge current}) \times (\text{discharge time})$$

The energy density (ED) of the film was determined by integrating the discharge curves between −0.6 V and −0.3 V. The average power density (PD) was obtained by dividing the ED by the discharge time.

*Theoretical Specific Capacity ($Q_{th}$).* The value of $Q_{th}$ corresponding to the cathode or anode material was calculated from

$$Q_{\text{th}} = \frac{nF}{M_{\text{w}}}$$

where $n$ is the number of moles of electrons corresponding to the reduction or oxidation of one mole of ABTS● or viologen, respectively and $M_w$ is the molecular weight of a repeat unit of pPy[ABTS] (1219.6 g/mol) or pPy-$V^{2+}$-Me (391 g/mol). The repeat unit was taken to be a

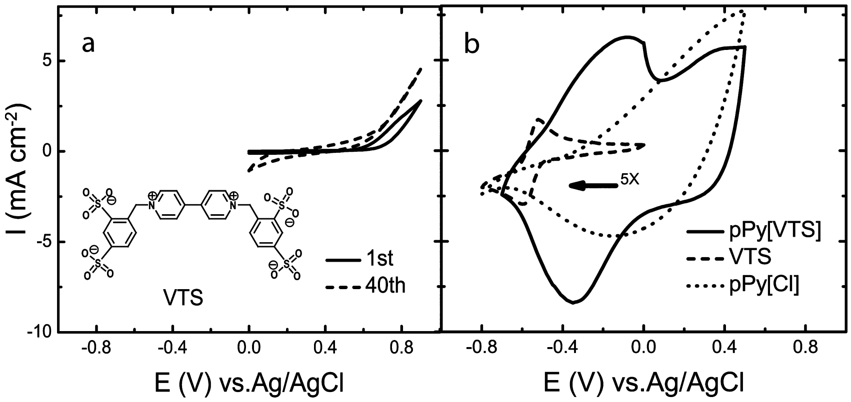


**Figure 2.** (a) Cyclic voltammograms obtained during the polymerization of 200 mM pyrrole in the presence of 25 mM VTS over 40 cycles at a scan rate of 100 mV/s (molecular structure of VTS shown in the inset). (b) Cyclic voltammograms of a pPy[VTS]-coated Au electrode immersed in 0.2 M KCl at a scan rate of 100 mV/s; corresponding cyclic voltammogram of 2.5 mM VTS in 0.2 M KCl at 100 mV/s (dashed line, enlarged by a factor of 5).

decamer of pyrrole units with a corresponding ABTS unit based on the 10:1 ratio of pyrrole to ABTS in these films.[39]

*Battery Experiments.* Films of the cathode (pPy[ABTS]) were synthesized following procedures described in our previous paper.[40] Films of the anode (pPy-$V^{2+}$-Me) were synthesized on a gold-coated silicon wafer (1 $cm^2$) using the previously described procedure. A battery was assembled in a two-electrode setup with pPY[ABTS] as the cathode, pPy-$V^{2+}$-Me as the anode, and 0.2 M $LiClO_4$/ACN as the electrolyte. Prior to discharge, the cell was charged potentiostatically for 150 s at +1.2 V (vs SSCE) and subsequently discharged at different current densities (between 0.25 mA $cm^{-2}$ and 5 mA $cm^{-2}$). The charge-carrying capacity of these films was determined from each discharge curve as

$$(\text{capacity}) = (\text{discharge current}) \times (\text{discharge time})$$

The ED value was determined by integrating the discharge curves between 1.2 V and 0.8 V. The average PD was obtained by dividing the ED by the discharge time.

## 3. RESULTS AND DISCUSSION

### 3.1. Sulfonate Derivatives of Viologen Electrostatically Trapped in Polycationic Polypyrrole.

Viologen is a dication when fully oxidized. Therefore, two viologen derivatives were synthesized with sulfonate groups to impart the anionic character necessary for electrostatic incorporation into polycationic pPy. The first viologen derivative investigated was a disulfonated viologen (VDS), 1,1′-bis(ethylsulfonate)-4,4′-bipyridinium dibromide, which was synthesized using a previously reported method.[77] Electropolymerization of pyrrole in the presence of VDS yielded a black film only when the applied potential was above 1.0 V (see Figure1b). This potential is higher than that used to electropolymerize pyrrole with other dopants.[78,79]

The presence of two quaternized N atoms on VDS was expected to have some impact on the rate of electropolymerization by pPy[VDS] via electrostatic repulsion with the polycationic backbone of a growing pPy chain. Growth of a conductive polymer film was indicated by an increase in peak current and capacitive response with repetitive cycling during the electrosynthesis of pPy[VDS] (Figure 1a). The redox peaks corresponding to both pPy and VDS components of pPy[VDS] are present at 0.05 V and −0.5 V, respectively, in the cyclic voltammograms shown in Figure 1b. However, the magnitude of the current corresponding to VDS in the film was not significantly larger than that of VDS in solution (shown as a dotted-line cyclic voltammogram). This result indicates that very little VDS is electrostatically bound to pPy during electrodeposition of pPy[VDS], despite the presence of two sulfonate moieties in the structure of VDS. The quaternized nitrogen atoms render this molecule neutrally charged under the conditions used to polymerize pyrrole; thus, a viologen with only two anionic moieties is not sufficient for codeposition with polycationic pPy. To overcome this limitation, a second viologen derivative was synthesized, specifically, the tetrasulfonated viologen (VTS) shown in Figure 2a and tested for its ability to be incorporated into electrodeposited pPy. The potential for the onset of polymerization of pPy[VTS] was 0.58 V vs Ag/AgCl, a more negative value than that needed to polymerize pPy[VDS] (i.e., 0.75 V vs Ag/AgCl).

Figure 2b shows the cyclic voltammograms of both solution VTS (dashed line, enlarged by a factor of 5) and an electrodeposited film of pPy[VTS] in monomer-free electrolyte (solid line). For comparison, the cyclic voltammogram of a film of pPy[Cl] is also shown. The reversible redox activity of VTS in a film of pPy[VTS] is evident at −0.35 V, which is not present in the cyclic voltammogram of pPy[Cl] electrodeposited under identical conditions. In addition, the higher current density (or $Q_{cv}$ from Table 1) of the electrodeposited film, compared to VTS in solution, indicates a high concentration of VTS within pPy[VTS].

### 3.2. Viologen Covalently Attached to Polycationic Polypyrrole.

In addition to synthesizing sulfonate derivatives of viologen, a derivative of viologen covalently attached to a pyrrole monomer (Py-$V^{2+}$-Me) was synthesized (Figure 3a).[74] This approach guarantees incorporation of viologen within the electrodeposited pPy film and relies on ions from the electrolyte for charge compensation. A cyclic voltammogram of the Py-$V^{2+}$-Me monomer in 0.2 M $LiClO_4$/ACN from 0 to +1.5 V revealed oxidation of *N*-alkyl pyrrole at an onset potential of 1.2 V (Figure 3a). The monomer was electropolymerized to yield a film of pPy-$V^{2+}$-Me. The alkyl linkage between the pyrrole and viologen reduces steric inhibition of electropolymerization by the pendant group and may provide the flexibility needed for high rates of self-exchange between oxidized and reduced forms of viologens.[68,80] Subsequent to polymer deposition, the electrode was rinsed and immersed in fresh electrolyte and a cyclic voltammogram taken, which revealed the reversible redox behavior of the pendant viologen ($V^{2+}/V^{+}$) centered at −0.5 V (Figure 3b).

Table 1. Electrochemical Properties of the Redox-Active Components in Solution or as a Component of the Polymer Film Coated on a Gold Working Electrode ($0.2\ cm^2$) in 0.2 M HCl

| polymers and monomers | $M_w$ (g/mol) | theoretical capacity, $Q_{th}$ ($mAh\ g^{-1}$) | voltammetric capacity, $Q_{cv}$ (nAh) at 100 mV/s |
|---|---|---|---|
| pPy[VDS] (10:1) | 1202 | 22 | 71 |
| VDS (2.5 mM solution) | 532 | 50 | 32 |
| pPy[VTS] (20:1) | 2154 | 13 | 1138 |
| VTS (2.5 mM solution) | 814 | 33 | 74 |
| pPy-$V^{2+}$-Me (1:1) | 391 | 68 | 2145 |
| Py-$V^{2+}$-Me, dichloride (10 mM ACN solution) | 391 | 68 | 165 |
| pPy[IC](10:1) | 1137 | 47 | 223 |
| IC (2.5 mM solution) | 466 | 115 | 67 |
| pPy[ABTS](10:1) | 1219 | 22 | 180 |
| ABTS (2.5 mM solution) | 548 | 49 | 33 |

The cyclic voltammogram shows a gradual increase in the cathodic and anodic peak currents, until they equilibrated after 100 cycles. As expected, the magnitude of the current or $Q_{cv}$ (Table 1) associated with the viologen in the polymer is significantly larger than that of the corresponding monomer in solution, indicating a high concentration of viologen in the polymer film. Given the relatively low conductivity of pPy ($<10^{-6}$ S/cm) in this potential range (−0.5 V to −1.0 V),[67,69,75,81] much of this charge transfer is the result of charge transfer between viologen units.

**3.3. Galvanostatic Discharge Tests of Films of pPy-[VTS] and pPy-$V^{2+}$-Me.** Films of pPy[VTS] and pPy-$V^{2+}$-Me subsequently were tested for their capacity to function as anodes in a polymer-based battery via galvanostatic discharging tests. Shown in Figure 4a are the results for a film of pPy[VTS]. The discharge plateau expected for VTS is not evident, but assuming a usable potential of −0.3 V for the anode, a capacity of 30 mAh/g was obtained with both viologen and polypyrrole contributing. The discharge curves of the pPy-$V^{2+}$-Me films at different current densities are shown in Figure 4b, which exhibit a distinct plateau in the discharge at −0.5 V. Significant capacity fading was observed at higher discharge rates due to the limited electronic conductivity of the pPy.[67,75,81] A maximum capacity of 55 mAh/g was observed at a current density of 0.25 mA/$cm^2$, which is 80% of its theoretical capacity (see Table 1).

Repeated charging and discharging experiments at 0.5 mA $cm^{-2}$ were performed to evaluate film stability, and the resulting change in capacity of both pPy[VTS] and pPy-$V^{2+}$-Me films is shown in Figure 4c, the latter retaining 70% of its initial capacity after 100 cycles. The 30% decrease in capacity is not due to an irreversible reaction between pyrrole and viologen,[63] but can arise through degradation of the polymer backbone or by irreversible chemical reaction of the reduced viologen with trace amounts of oxygen present in the system.[41,46,63] Both viologen films proved to be less stable with repeated charging and discharging relative to an anode consisting of pPy doped with indigo carmine (pPy[IC]) in the absence of a rigorous exclusion of oxygen.

**3.4. Performance of Battery with pPy-$V^{2+}$-Me Anode and pPy[ABTS] Cathode.** Of the three polypyrrole−viologen composites tested, the covalently linked pPy-$V^{2+}$-Me exhibited the best discharge curve and highest capacity. Thus, a battery was prepared using pPy-$V^{2+}$-Me as the anode material and pPy doped with 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) (pPy[ABTS]) as the cathode material. Discharge curves of this battery are shown in Figure 5a, which exhibit a plateau discharge at 1.0 V. Based on the values determined for each electrode material (Table 1), the theoretical capacity of a battery consisting of an anode of pPy-$V^{2+}$-Me and a cathode of pPy[ABTS] is 17 mAh/g. Experimentally, this battery exhibits an open circuit voltage of 1.2 V, and a maximum capacity of 16 mAh/g at 800 mV and 0.1 mA/$cm^2$ load. Interestingly, the rate of capacity loss from repeated charging and discharging was found to be slower when the pPy-$V^{2+}$-Me film was tested in a battery configuration (e.g., pPy-$V^{2+}$-Me)||pPy[ABTS]) compared to the half-cell (e.g., pPy-$V^{2+}$-Me anode), although both exhibited similar levels of capacity loss after 100 cycles (see Figure 4c).

Performance characteristics of the pPy-$V^{2+}$-Me||pPy[ABTS] battery were further compared to the pPy[IC]||pPy[ABTS] battery reported earlier using a Ragone plot (Figure 5b). Both batteries retain a fairly constant energy density (ED) at power densities up to $10^4$ W/kg. The pPy-$V^{2+}$-Me||pPy[ABTS] battery exhibits a maximum ED of 15 Wh/kg, which is slightly

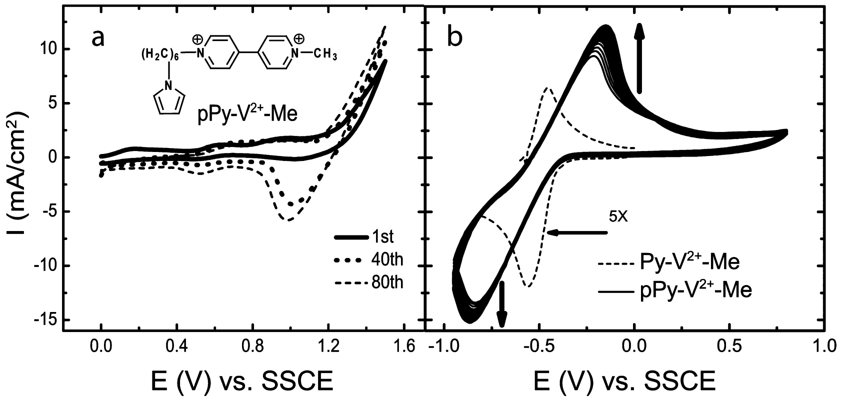


Figure 3. (a) Cyclic voltammograms obtained during the electropolymerization of 10 mM Py-$V^{2+}$-Me in the presence of 0.2 M $LiClO_4$/ACN over 80 cycles between 0 and 1.5 V vs SSCE at a scan rate of 100 mV/s (molecular structure of the Py-$V^{2+}$-Me monomer in the inset); (b) cyclic voltammograms of a Au electrode coated with pPy-$V^{2+}$-Me repeatedly scanned (100 cycles) at a scan rate of 100 mV/s in 0.2 M $LiClO_4$/ACN. For comparison, the CV of a 10 mM solution of Py-$V^{2+}$-Me (dashed line, image enlarged by a factor of 5) in 0.2 M $LiClO_4$/ACN.

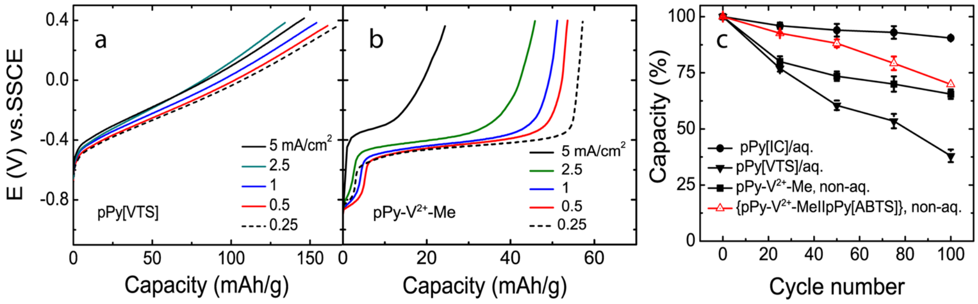


**Figure 4.** (a) Discharge curves of pPy[VTS] in aqueous 0.2 M KCl after charging for 300 s at −0.7 V vs Ag/AgCl (potential reported vs SSCE); (b) discharge curves of pPy-$V^{2+}$-Me in 0.2 M $LiClO_4$/ACN; (c) and change in capacity of the different systems tested during repeated charging−discharging at 0.5 mA $cm^{-2}$.

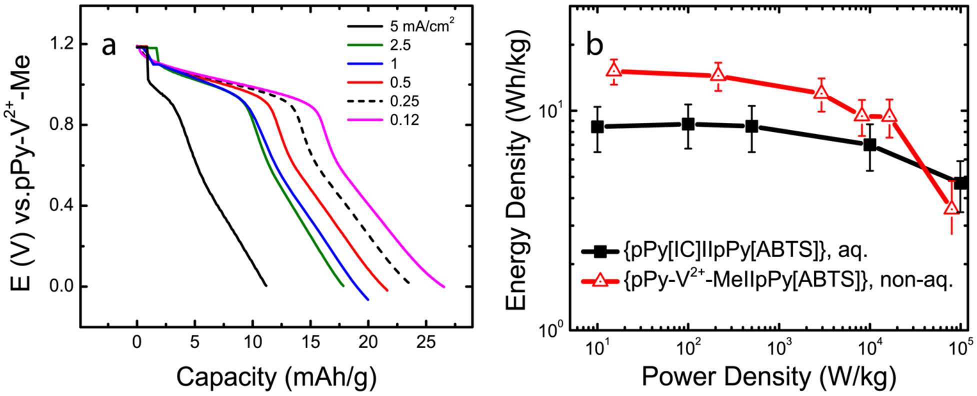


**Figure 5.** (a) Discharge curves of a battery consisting of a pPy-$V^{2+}$-Me anode and a pPy[ABTS] cathode in 0.2 M $LiClO_4$/ACN. (b) Ragone plot comparing two battery systems: pPy-$V^{2+}$-Me||pPy[ABTS] and pPy[IC]||pPy[ABTS].

higher than the pPy[IC]||pPy[ABTS] battery reported previously.[39]

## 4. CONCLUSIONS

Viologens were studied as dopants in polypyrrole films for the purpose of increasing charge storage capacity of the film at more-negative voltages. Both electrostatic and covalent incorporation of viologen into polypyrrole films were studied. The resulting materials were tested as anodes for an all polymer-based battery. Poor films were electrodeposited when a disulfonated viologen was used as an electrostatic dopant, as indicated by a small increase in $Q_{cv}$ of the polymer compared to the dopant in solution. Electrodeposited films improved significantly when a tetra-sulfonated viologen was used as the electrostatic dopant, as determined by analysis of the cyclic voltammogram and discharge curves. Electrodeposited films consisting of viologen covalently bound to the polypyrrole backbone exhibit the highest capacity and best cycle life of the three materials studied principally due to the 1:1 ratio of viologen units to pyrrole units in polymer (electrostatically bound dopants typically are at a ratio of 1 dianionic dopant per 10 pyrrole units). As an anode material, pPy-$V^{2+}$-Me exhibits a distinct faradaic discharge plateau at −0.5 V, corresponding to the $V^{2+}/V^{+}$ redox couple. A battery with an emf of 1.0 V was demonstrated when a pPy-$V^{2+}$-Me anode was coupled with a pPy[ABTS] cathode. This battery retained a capacity of 70% after 100 charge−discharge cycles and a maximum ED of 15 Wh/kg. Both the covalent and electrostatic approaches can be used to concentrate and immobilize viologens within a conductive polymer. The resulting composites provide a route to increasing the cell emf and capacity of polymer-based batteries.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the National Science Foundation (Grant Numbers: HRD-0548311, CBET-1159255, and CHE-1240020). S.S. is grateful to the Electrochemical Society for an Edward G. Weston summer research fellowship.

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