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Beyond solubility: Mechanistic understanding of Redox-activity loss in Diethyl and Diheptyl Viologens in non-aqueous and ionic liquid-based electrochemical capacitors

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ABSTRACT

Viologen-based redox electrolytes are recognized for their two-electron redox process, and low self-discharge characteristics without ion-exchange membrane. However, their electrochemical performance has not yet been fully realized, as only the first redox couple, i.e., dicationic species (V^{2+})/monocation radical (V^{+}), is typically utilized in practical energy-storage devices. The second redox couple, corresponding to the V^{+}/neutral dialkylbipyridinylidene(V°) is generally not realized because of low electrochemical window of the aqueous electrolytes, the poor solubility of V°, and its tendency to undergo dimerization and aggregation in the non-aqueous electrolytes. To address these limitations, molecularly engineered viologen derivatives containing permanently charged substituents or extended π-conjugated moieties have been developed to increase the solubility of V^{0} and reduce its dimerization and aggregation . Nevertheless, several studies have reported stable utilization of the second redox couple even for simple dialkyl viologen derivatives. These seemingly contradictory observations necessitate a systematic re-examination of the accessibility, reversibility, and long-term stability of the second redox couple in viologens. In the present work, we have systematically evaluate the beaviour of diethyl and diheptyl viologen derivatives with bromide and hexafluorophosphate counnterions in acetonitrile (ACN), ionic liquid (IL) and their mixtures. Electrochemical investigation reveal that the irreversible redox failure of these redox additives in ACN and IL/ACN, highlights the limitations of simple viologen derivatives. A possible mechanism for the observed failure is proposed based on the synergistic correlation between zero-charge voltage, the potential attained by the negative electrode during electrochemical measurement in the full cell, and the stability of the two redox couples of the bipyridinium ion, as determined from half-cell measurement. Additionally, FTIR, UV, and XPS analyses were employed to provide evidence supporting the proposed mechanism.

1. Introduction

Coventional, electrical double layer capacitors have been overshadowed by electrochemical capacitors due to their high specific energy. The integration of redox electrolyte in the capacitors is one of the simple ways to fabricate electrochemical capacitors [1]. The availability of plenty of redox-active compounds offers the flexibility to device fabrication [1–21]. Reversible electrochemical redox process of these mono-functional redox additives improves performance of either the positive or the negative electrode and thus enhances the specific energy of the full cell. However, the absence of a balancing redox activity at the second electrode and redox-shuttling induced self-discharge limit the full advantage of this simple approach. Recent studies have established the effectiveness of combining two suitable mono-functional redox

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additives in an electrolyte for electrochemical capacitors [15,22–24]. Self-discharge due to crossover of the redox species can be mitigated by using an ion-exchange membrane or a combination of two solid redox electrolytes. These approaches have suffer either the high cost of the membrane in the fluid electrolyte or poor mass transport in the solid electrolyte.

Recently, Chun et al. [13] have designed high-energy electrochemical capacitors with low self-discharge without an ion-exchange membrane by using 0.5 M viologen/1.0 M $KBr_{(aq.)}$ electrolyte. Sathyamoorthi et al. proposed viologen dibromide as a single organic redox species, acting as a bifunctional (dual) redox electrolyte for supercapacitors [8]. Also, time-dependent confinement of viologen on a carbon electrode was demonstrated using electrochemical techniques [8]. Further, Evanko et al. [2] elucidated that the confinement results from mutual complexation between the monocation radical (V^{+}) and bromide anion in the carbon pore.

Viologen is recognised for its high energy storage capacity due to involvement of two redox couples through a two-step redox process, i.e., dication (V^{2+})/ mono cation radical (V^{+}) and V^{+}/neutral dialkylbipyridinylidene (V°) [25]. So far, the contribution of the first redox couple (V^{2+}/V^{+}) in the aqueous electrolyte has been extensively investigated for an electrochemical capacitors [2,8,13] and redox flow batteries [25–35]. The narrow electrochemical window of aqueous electrolyte and the poor solubility of the V° in aqueous electrolyte restrict the utilization of the second redox couple. In supercapacitors with activated carbon (AC) electrodes, H_2 evolution starts at −0.3 V vs. NHE in acidic and neutral electrolytes, before the onset of the second redox step of viologen (V^{+}/V°). In redox flow batteries, possibly the poor solubility of V^{0} in aqueous solution [36] restricts the utilization of the second redox couple, although graphite electrode offers a wide electrochemical window.

To address the poor solubility of V^{0}, moleculary engineered viologen derivatives were used as new redox species. DeBruler et al. [37] introduced viologen derivatives with permanently positively charged ammonium functionalities in the viologen structure, resulting in a charged viologen species even after the second redox step. The hydrophilicity of the reduced species increases the solubility, and the charged nature prevents dimerization and aggregation [37]. Luo et al. [9] demonstrated a dual-redox electrochemical capacitor using viologen derivatives containing permanently charged substituents. Another strategy for the stable utilization of the second redox couple involves the extended π-conjugated viologen derivatives, which has been demonstrated in both redox flow batteries and electrochemical capacitors [38, 39]. Nevertheless, several studies have reported stable utilization of the second redox couple even for simple dialkyl viologen derivatives [40–42]. Suh-Eun Hyeon et al. [40] reported a stable electrochemical supercapacitor using a viologen redox additive in an aqueous zwitterionic gel electrolyte. Similarly, Vijayan et al. [41] reported an electrochemical supercapacitor using viologen as adual-redox specie in KOH electrolyte, surprisingly exhibiting 93% capacitance retention after 10, 000 charge-discharge cycles. These reports simply overlook the solubility of V^{0} in aqueous medium and its tendancy to undergo dimerization/aggregation. In addition, the degradation of viologen through dealkylation in strong alkaline media such as KOH is well documented [43]. Hu et al. [42] reported two-electron utilization of viologen in the non-aqueous solvent acetonitrile (ACN) using a viologen moiety with a hydrophobic TFSI anion. Although organic solvents improve the solubility of the viologen species with a hydrophobic anion, dimerization or aggregation of V° can not be prevented [36,44].

These conflicting views in the literature on viologen-based redox systems necessitate a reexamination of their electrochemical behaviour and stability. The present work investigates the second redox step of viologen in non-aqueous media and ionic liquid for application in electrochemical capacitors. Two types of commonly employed dialkyl-substituted viologen redox species dual-functional viologen dibromide and mono-functional viologen hexafluorophosphate,are studied [2,8, 13]. In addition, a full cell with a reference electrode in the spectator mode is used to monitor the voltage development of positive and negative electrodes during the charge-discharge cycling. The specially designed cells with transparent glass housing are fabricated to monitor the formation of radical cation in a real time through the colour change of electrolyte.

2. Experimental section

2.1. Electrolytes

Ionic liquid (IL), 1-allyl-1-methylpiperidinium bis((trifluoromethyl) sulfonyl)imide, was synthesized accroding to the reported procedure [45]. The moisture content of IL was estimated as <100 ppm by using a Metrohm 899 Karl Fischer coulometer. The bifunctional viologen redox additives, namely diethylviologen dibromide (EVBr), diheptylviologen dibromide (HVBr) and the mono-functional diheptylviologen bis(hexafluorophosphate) ($HVPF_6$), were synthesized accroding to the reported procedure [8,46] (ESI). Redox-active electrolytes were prepared by dissolving $HVPF_6$, EVBr and HVBr in neat IL, ACN and their mixture at different concentrations (wt. %).

2.2. Carbon electrodes

Activated carbon (AC) (Ranbaxy Chem. India Pvt. Ltd.), binder polyvinylidene difluoride (PVDF) (Sigma-Aldrich), and the solvent, N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich), were used to prepare the AC electrodes. The specific surface area of 954 $m^2 \cdot g^{-1}$ (Brunauer-Emmett-Teller (BET)) and the total specific pore volume of 0.59 $mL \cdot g^{-1}$ were obtained for AC using nitrogen gas sorption measurement with Quantachrome Autosorb IQ station 1 [17]. The carbon paste was prepared by dispersing AC in NMP, followed by the addition of PVDF/ NMP (10 wt.%). Smoothly polished stainless steel (SS) circular current collectors with an area of 1.5 cm^2 and 0.8 cm^2 were used to make carbon electrodes for 2 and 3-electrode configurations, respectively. The carbon paste was coated onto the SS current collector and dried at 120 °C for 30 min.

2.3. Fabrication of supercapacitor

A supercapacitor was fabricated in a glove box (Mbraun) with a moisture content < 10 ppm, as described in previous report [8]. Symmetrical supercapacitors were constructed using a Teflon cell housing with a Swagelok fitting and a 3 mm SS cylindrical current collector. A T-shaped perfluoroalkoxy (PFA)-Teflon Swagelok cell body fitting with the SS cylindrical current collector was used to fabricate the three-electrode configuration. Also, a T-shaped symmetrical supercapacitor with a reference electrode in the spectator mode was also used to monitor the potential development of both electrodes. A polypropylene separator and an Ag/AgCl quasi_reference electrode were used. Active mass loading of ~8.5 mg and ~4.0 mg of AC for an electrode were used in the two- and three-electrode configurations, respectively. An overloaded counter electrode were used in the three-electrode configuration to suppress the unintended electrochemical process at the counter electrode. The electrochemical redox processes resulted in the formation of coloured redox species on both positive and negative electrodes, allowing their formation to be tracked by visual observation. For the real-time colour monitoring, an electrochemical cell with a transparent glass-housing was designed to observe the colour change during the electrochemical measurements.

2.4. Electrochemical characterization

Cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL) at pre-defined cell voltages were carried out for the supercapacitor with redox-active and inert electrolytes using an Autolab

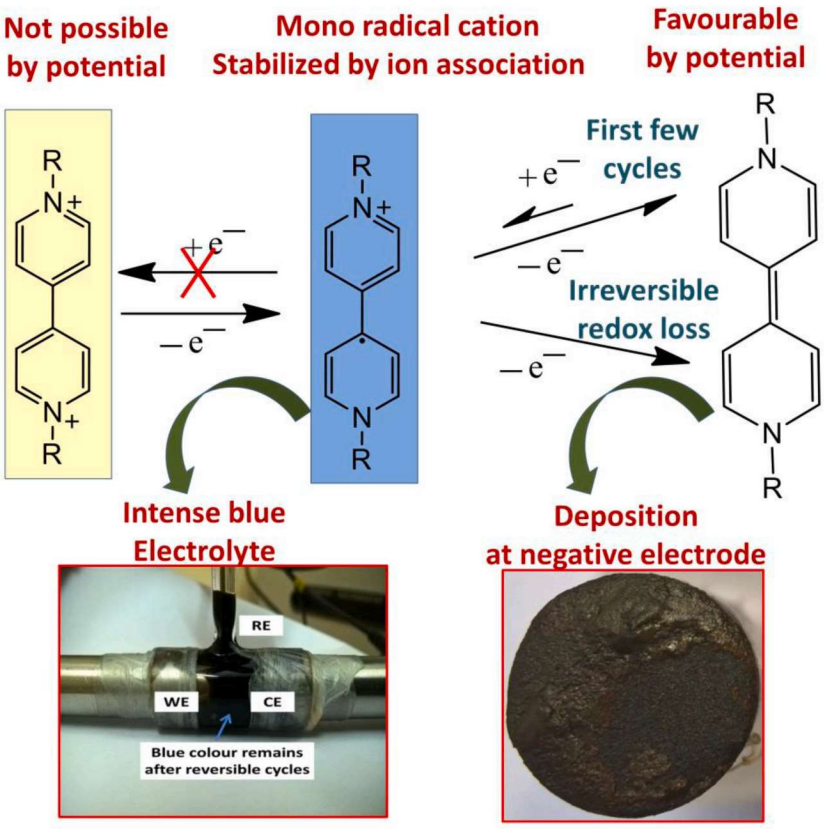
reference electrode was identified as the E_0 for the cell voltage of 2.0 V, and further, the E_0 remains the same throughout the measurement.

The maximum voltage development on the positive electrode is 0.6 V, while that at the negative electrode is −1.4 V vs. Ag/AgCl quasi-reference electrode. Interestingly, the potential of −0.2 V corresponds to the peak potential for the first reduction process, which is very close to the E_0 (Fig. 6A). Also, the oxidation of neutral V^0 to $V^{+\cdot}$ and subsequently to V^{2+} starts at −0.4 V and is completed at 0.7 V (Fig. 6A). Hence, the oxidation of dialkylbipyridinylidene is not possible i on the negative electrode, resulting in the irreversible failure of the redox activity of HVBr. To verify this claim, continuous CV was performed with three electrode configuration in the potential window corresponding to the potential development on the negative electrode (0 to −1.2 V vs. AgCl quasi-reference electrode) until the disappearance of redox activity of the electrolyte (Fig. 8B). Real-time colour change during multi CVs is shown in Fig. S7. The formation of blue and yellowish brown colour in and around the working and counter electrodes indicate the redox process of bipyridinium and bromide ions. It is very clear from the CV profile that the redox couples of viologen do not operate in the voltage window of the negative electrode (ie. the oxidation and reduction of the redox couples), which seriously affects the reversibility of the redox reaction.

A partial reduction peak started at 0 V and a broad reduction peak at −0.78 V was noted on the negative sweep. Similarly, a partial oxidation peak starting at −0.6 V on the positive sweep in the first cycle was observed. However, the first reduction peak was not observed in the second cycle, corresponding to the reduction of V^{2+} to $V^{+\cdot}$ radical indicating the unavailability of the V^{2+} for the electrochemical reduction. This may be due to the voltage development of the negative electrode, which favours the oxidation of V^0 to $V^{+\cdot}$, and further oxidation of $V^{+\cdot}$ to V^{2+} becomes impossible. Also, the stabilization of $V^{+\cdot}$ in the IL/ACN medium prevents the formation of V^{2+} via disproportionation of $V^{+\cdot}$ radical to V^{2+}, which results in the accumulation of monocation radical near the electrode-electrolyte interface and in the electrolyte [36]. The complete disappearance of redox activity was noted on the 10th cycle, which is due to the voltage development on the working electrode (negative electrode in the full cell) favouring the second redox couple ($V^0/V^{+\cdot}$). Further, the concentration of monocation radical increases on subsequent sweeps, favouring the reduction to neutral V^0. The resultant insoluble and non-porous deposit of neutral V^0 on the working electrode blocks the diffusion of ions, which results in poor double-layer capacitive behaviour on 15th cycle. The electrochemical process at the negative electrode is depicted in Scheme 1. All these factors contribute to the irreversible redox failure of redox activity of the HVBr in theIL/ACN. The present results highlight the challenges associated with using simple viologens for stable two-electron redox utilization in supercapacitors. Viologen structures with permanent charges or suitable substituents may improve the solubility of reduced species and reduce radical association. Solvent and electrolyte composition also need to be considered, particularly with respect to viscosity, polarity, ionic-liquid composition, and counterion effects. These factors can influence the transport, association, and deposition of reduced viologen species. Thus, both viologen structure and electrolyte composition should be optimized to achieve more stable two-electron utilization and improved cycling performance.

4. Conclusions

We have systematically evaluated the possibility of bifunctional viologen redox electrolyte for high-voltage activated carbon-based electrochemical capacitors. Mono-functional viologen redox electrolytes such as $EVPF_6$ and $HVPF_6$ in ACN were not suitable for high-



Scheme 1. The electrochemical process is depicted at the negative electrode from 0 to −1.2 V vs. $Ag/AgCl_{quasi}$ corresponds to the voltage development in the full cell at the cell voltage of 2.0 V. The optical image of the electrode with deposition and the intense blue colour of the electrolyte by the stabilization of $V^{+\cdot}$ radical by ion association in HVBr/IL/ACN are shown.

voltage supercapacitors, as voltage development on the positive electrode limited the cell voltage. The EVBr/IL improved the performance by Faradaic contribution, however, the longevity of the EVBr/IL was poor and almost disappeared after 600 GCPL cycles at 1.0 $A{\cdot}g^{-1}$. The solubility of HVBr and EVBr was improved using IL/ACN. The supercapacitors with these electrolytes exhibited rapid capacity fading, with the redox activity of HVBr and EVBr in IL/ACN disappearing completely after only a few GCPL or CV cycles. A mechanism of the disappearance of redox activity was comprehensively studied using the electrochemical methods, FTIR, UV and XPS characterization. The E_0 and the voltage development on the negative electrode in the full cell from GCPL favoured the less reversible redox couple $V^0/V^{+\cdot}$ over the completely reversible redox couple $V^{+\cdot}/V^{2+}$. Further deposition of insoluble deposit on the negative electrode was noted on the recovered negative electrode after the multi-CV of the half-cell. The FTIR analysis confirms the chemical integrity of the viologen framework after multicycle experiments. The presence of $V^{+\cdot}$ is evident in the blue-coloured electrolyte solution. Furthermore, XPS analysis confirms the presence of partially reduced and fully reduced viologen species in the deposit. The irreversible redox failure of redox activity was confirmed by the CV between E_0 and −1.2 V vs. $AgCl_{quasi}$. It was explained by the interconnection of E_0, the voltage development on the negative electrode in the full cell and the stability of two redox couples in half-cell configuration. The observed instability not only restricts their practical applicability in high-voltage energy storage devices but also validates requirement for structural modification or advanced molecular engineering to overcome these fundamental shortcomings.

Ethical approval

Not applicable.

Availability of data and materials

All data used in the research work are given in the manuscript

CRediT authorship contribution statement

S. Sathyamoorthi: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M. Kanagaraj:** Investigation. **A. Kumaravel:** Writing – review & editing. **Murugavel Kathiresan:** Writing – review & editing, Investigation. **V. Suryanarayanan:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2026.150032.

Data availability

All data generated during this study are included in the published article and its Supporting Information.

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