Approaches to Electrolyte Solvent Selection for Poly-Anthaquinone Sulfide Organic Electrode Material

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Organic materials such as polyanthraquinone sulfide (PAQS) are receiving increased attention as electrodes for energy storage systems owing to their good environmental compatibility, high rate capability, and large charge-storage capacity. However, one of their limitations is the solubility in organic solvents typically composing the electrolytes. Here, the solubility of PAQS was tested in 17 different solvents using UV/Vis spectroscopy. The results show that PAQS exhibits a very wide range of solubility according to the nature of the solvent and the obtained trend agrees well with the predictions from Hansen solubility analysis. Furthermore, the transport properties (conductivity, α, and viscosity, η) of selected electrolytes composed of non-solubilising solvents with 1 M LITFSI are compared and discussed in the temperature range from −40 °C to 80 °C. In the second part of this study, the electrochemical characterization of PAQS as electrode material in selected pure or mixture of solvents with 1 M LITFSI as salt was made in half-cells by a galvanostatic method. In a methylglutaronitrile (2MeGLN)-based electrolyte that exhibits low solubility of PAQS, it appears that the capacity fade is intricately linked to the large irreversibility of the second step of the redox process. Although the standard cyclic carbonate solvents mixture (ethylene carbonate and propylene carbonate) led to rapid capacity fade in the initial 10–15 cycles owing to their high solubilising ability. Finally, it is shown that a pure linear alkylcarbonate (dimethyl carbonate) or binary mixture of ether-based (dioxolane/dimethoxy ethane) electrolyte is much more compatible for enhanced capacity retention in PAQS with more than 120 mAh g⁻¹ for 1000 cycles at 4 °C.

Introduction

In the last decade, the global production of energy storage devices is experiencing exponential growth owing to the increasing demand for electric vehicles, grid scale storage, and portable electronic devices. The currently used battery technologies, which include nickel cadmium, nickel metal or Li-ion batteries rely heavily on mining activities that raise concerns about their long-term environmental impact.[1] In conventional Li-ion batteries, the cathode and anode (lithium titanate) materials require a large quantity of mined elements such as Ni, Mn, Co, Ti, and the safe disposal or reuse of these elements poses significant technical challenges as the volume of global battery manufacturing continues to increase.[2] As a result, several organic redox materials that are mainly composed of elements such as O, C, N, and S are being investigated as suitable substitutes.[3] Owing to the open structure of the organic materials, they are not constrained by cation sizes and as such can reversibly incorporate ions of widely varying ionic radii [Li⁺, Na⁺, K⁺, Cs⁺, Mg⁺, tetraethyl ammonium (TEA⁺)].[4–6] Most of the organic materials exhibit low overpotentials even at high cycling rates (>4C), which make them suitable for energy storage applications in which high power density is required.[7,8] Depending on the redox functional group, the organic electrodes may be classified into organosulfur, carbonyl, conjugated polymers, and amines.[9,10,7] A large number of carbonyl-containing redox materials have been widely investigated in the last few decades owing to their relatively large (100–600 mAhg⁻¹) and reversible capacity.[11–13]

On the downside, there are two major challenges that need to be resolved: 1) high capacity fade primarily owed to the solubility of the active material and 2) low electronic conductivity. The issue of solubility requires the design of suitable electrolytes in which the solubility can be minimized. A major improvement can be achieved also by polymerization of the electrochemically active monomers by which the solubility is considerably reduced. In the case of anthraquinone (AQ), the polymerization using C=S or C=C linkages or attaching the AQ as pendant to a stable polymer backbone can be used to produce long-chain length polymers that exhibit a substantially improved capacity retention over long cycling.[14,15] A polymer of this type, polyanthraquinone sulfide (PAQS), which is formed by the polymerization reaction of 1,5-dichloroanthraquinone (DCAQ) with Na₂S is widely investigated.[6,4] The redox potential of this polymer is ≈2.1 V versus Li/Li⁺ with a relatively flat voltage profile. Most of the reported studies focusing on the performance of PAQS are conducted in half cells with the appropriate metal foil as the anode (Li, Na, K).,[16,13] However, in a recent study, the use of PAQS as anode material in an all-organic battery with polytriphenylamine (PTPA) cathode was pro-

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Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/cssc.201701962.

DOI: 10.1002/cssc.201701962
Based on the redox potential of PAQS, it may be suitable for use with several conventional Li-ion intercalation cathodes. Compared to the graphite anode (≈ 0.1 V vs. Li/Li⁺), PAQS lies well within the potential range of the electrolyte stability of conventional carbonate electrolytes while offering advantages of fast reaction kinetics. In that sense, it may be seen as an environmentally benign substitute for the “zero strain” anode material lithium titanate (LTO, 175 mAh g⁻¹), which is also immune to solid-electrolyte interface (SEI) formation and has been demonstrated to have excellent rate capability (1.55 V vs. Li/Li⁺).³⁻¹⁸

The problem, however, with such a battery is that the ether-based electrolyte solvents in which PAQS is tested are known to be susceptible to rapid decomposition at high oxidative potentials at which the common cathode materials operate.³¹⁻¹⁹

The alkyl carbonates,²⁰ dinitriles,²¹ and some lactones as γ-BL²² show excellent anodic stability and have been proposed as battery electrolyte solvents.²²⁻²⁴ By comparison, all ether-based solvents such as THF, 2-methyltetrahydrofuran (2MeTHF), dioxolane (DOL), dimethoxy ethane (DME) exhibit much lower anodic stability.²⁰⁻²⁴ To address this limitation, we explored the compatibility of PAQS with several electrolyte systems that are known to have higher anodic stability starting with the conventionally used alkyl carbonates, lactones, and dinitriles.²⁰

Here, we first measured the solubility of PAQS in several pure solvents using UV/Vis spectroscopy to obtain a general understanding of the solubility of this polymer. Then, we selected some candidate solvents for electrolyte formulation followed by physical (viscosity and conductivity) and electrochemical characterization. The effect of the solvent nature on the electrochemical reversibility and capacity retention of PAQS was compared.

Results and Discussion

The PAQS material consists of monomers of anthraquinone connected with thioether linkages as shown in Scheme 1. The synthesis by polycondensation of DCAQ with Na₂S was characterised by FTIR (Figure S4b in the Supporting Information) and the obtained spectrum is similar to previously published studies.⁶⁻¹⁶⁻²⁵ The peaks at 1667 and 1567 cm⁻¹ are ascribed to the C=O and C=C bonds in the anthraquinone unit. The peaks at 1410 and 1128 cm⁻¹ correspond to the stretching vibrations of the sulfur-disubstituted aromatic ring and the ring-sulfur, respectively, and are direct evidence for the successful polymerization reaction. The obtained Raman spectra confirm the expected surface characteristics and the phase purity of the material, as previously data reported for this material.²⁶ The peaks at 1177, 1570, and 1642 cm⁻¹ (Figure S4a) correspond to in-plane C–H bending vibrations, symmetric stretching of sulfur-disubstituted ring and C=O stretching vibrations, respectively.

The initial potential (OCV) of a pristine PAQS electrode with reference to Li/Li⁺ is typically 2.8–3.0 V. As the material is electrochemically reduced it undergoes a two-step (steps I and II) reduction process in which the carbonyl oxygen atoms attain unit negative charge, which is suitably balanced by cations inserted from the electrolyte to maintain overall the charge neutrality (shown in Scheme 1).³¹ As a result, the process of discharge, reduction, and alkali cation insertion are analogous. Owing to the proposed usage of PAQS as an anode in full cells, in this text we will describe the redox process in terms of reduction/oxidation and PAQS in terms of reduced/oxidized state, to avoid confusion.

PAQS solubility evaluation in selected solvents by UV/Vis spectroscopy

For evaluating the solubility of PAQS in a wide spectra of selected solvents, a measured quantity of PAQS (50 mg) was added to the respective solvents and maintained in a temperature-controlled oven at 40 °C for 48 h. This time was sufficient to allow any undissolved particles to settle down at the base of the vessel leading to a clear supernatant, which was used for UV/Vis spectroscopy. The large difference in the solubility in various solvents can be clearly observed visually from the image shown in Figure S2.

The solvents selected for this study included the standard solvents for batteries as well as number of compounds such as ethanol and acetone, which are not suitable as electrolytes for Li-ion battery but were included to develop a comprehensive picture of the solubility. The structural properties as Van der Waals volume and charge density profile of select solvents of interest in this study are presented in Table 1. The size of the solvents can be a determining parameter if one considers the 3D lacunar structure of the PAQS. On the other hand, the charge distribution on the solvent molecule can influence the stability of the ionic or radical C–O fragment during the redox processes, so it is important to take them into consideration for subsequent discussion.

In Figure 1, the obtained absorbance values as a function of the wavelength in the range of 350–700 nm are shown for the 17 solvents. A broad peak at 450 nm corresponding to PAQS that was consistently observed in all solvents was treated as the reference wavelength for comparing absorbance values. The absorbance, A, at λ_ref = 450 nm is directly proportional to the concentration of the absorbing species and is a direct indicator of the concentration of solute across solvents.

Based on the peak absorbance values at the reference wavelength, the solvents can be categorized as indicated by the

![Scheme 1. Redox reaction of PAQS involving a two-step reduction/oxidation.](https://example.com/scheme1.png)
The dipole moment (\(D\)) and dielectric constant (\(\varepsilon\)) of the various solvents are summarized in Table 2. By comparing the absorbance values and the physical properties of the electrolytes it is clear that the trends in solubility cannot be readily explained by the dielectric constant or the dipole moments of the solvents alone. For example, DMF, \(\gamma\)-butyrolactone (\(\gamma\)-BL) and GLN have similar dielectric constants (\(\approx 37-39\)) but the solubility of PAQS in DMF is almost 25\(\times\) that in GLN and 2.5\(\times\) that in \(\gamma\)-BL.

The trend in solubility can be better explained by using the Hansen solubility parameters (HSP), which have been successfully applied in the design of industrial solvents.\(^{27}\) The HSP theory divides the cohesive energy of intermolecular interactions of solvent/solute molecules into three components, namely, \(\delta_h\) (hydrogen bonding), \(\delta_d\) (dispersive interaction), and \(\delta_p\) (polar cohesive energy) contributions.\(^{27}\) The HSPs for all solvents considered here were obtained from literature and are listed in Table S1. According to the theory, the solubility can be treated as the collective effect of the three aforementioned intermolecular interactions. The distance in Hansen space (\(R_i\)) for a solvent/solute pair is calculated as follows [Eq. (1)]:

\[
(R_i)^2 = 4(\delta_{h2} - \delta_{d1})^2 + (\delta_{d2} - \delta_{h1})^2 + (\delta_{p2} - \delta_{p1})^2
\]  

(1)

The value of \(R_i\) is indicative of the tendency of a solvent to dissolve the solute; a smaller value of \(R_i\) indicates a higher solubility. The calculated \(R_i\) values as per the above equation are listed in Table 2. The HSPs for all solvents are also represented
in 3D space in Figure 2 and color-coded into the following three categories for the benefit of the reader: $R_i < 7$ (red), $7 < R_i < 10$ (blue), and $R_i > 10$ (green). Solvents that are closer to PAQS appear in red and correspondingly have high solubility for PAQS.

![Figure 2](image-url) Location of selected solvents in Hansen space, color coded into the following three categories: $R_i < 7$ (red), $7 < R_i < 10$ (blue), and $R_i > 10$ (green).

From the obtained values, it can be seen that the HSP can accurately predict the trend in solubility. The $R_i$ for water is the highest by far (31.93 MPa·Å$^2$), which agrees well with the observation of insolubility from UV/Vis results. DMF, DMSO, and γ- BL, which were observed to have high solubility, have very small $R_i$ values of 1.77, 1.97, and 4.30 MPa·Å$^2$, respectively. Within the family of carbonate solvents, the linear alkyl carbonates have higher $R_i$ values compared to cyclic carbonates, which also agrees well with the observed solubility trend (PC > DMC). In ether solvents, the exception is 1,4-dioxane, which has a higher $R_i$, compared to DME but also has higher solubility. Although we have not tested yet with any other organic redox materials, this strategy could be generally applicable for the selection of suitable solvents for a wide variety of organic electrode materials.

Based on the observation of low solubility, we selected 2-MeGLN and DEC for further evaluation whereas γ-BL was not considered further due to the high solubility for PAQS. Owing to their widespread use in commercial devices we chose to investigate three different compositions of alkyl carbonates (EC/PC/DMC = 1:1:3, 1:1:5, 1:1:7, 1:1:9, 0:0:1 wt%). The chemical structure, molecular volume and charge density of all solvents of interest are shown in Table 2.

The peak absorbance values ($A$) from UV/Vis spectroscopy for a range of EC/PC/DMC solvent mixtures containing dissolved PAQS are plotted as a function of the wt% of DMC in the solvent mixture in Figure 3. Because the solubility of PAQS is inversely related to the Hansen distance, the $1/R_i$ values are plotted on the vertical axis (right). It can be seen that as the DMC content increases up to 100%, the solubility of PAQS decreases in the electrolyte along with the $1/R_i$ values.

![Figure 3](image-url) Correlation between peak absorbance values obtained from UV/Vis spectroscopy for selected EC/PC/DMC (1:1:3, 1:1:5, 1:1:7, 1:1:9, 0:0:1 wt%) and calculated inverse Hansen distance ($1/R_i$) for a range of compositions.

These results indicate that there is a direct relationship between the solubilizing ability and the presence of cyclic alkyl carbonates. This result will be revisited in a following section dealing with electrochemical testing in the EC/PC/DMC electrolytes.

**Physical characterization of electrolytes**

As the physical characterization of EC/PC/DMC mixtures has been extensively reported previously, we limit the physical characterization measurements to the four compositions shown in Figure 4(a). The conductivity was measured in the temperature range of −40 °C to 80 °C at an interval of 1 °C and the obtained results are shown in Figure 4a. All the reported electrolytes contained 1 M LiTFSI, henceforth, the electrolytes are referred to by the organic solvents. Over a majority of the temperature range, the conductivity follows the following trend: DOL/DME > DMC > DEC > 2MeGLN. At 25 °C, the conductivity of DOL/DME electrolyte is 24.66 mS cm$^{-1}$, which is about 10$\times$ higher than the 2-MeGLN- and DEC-based electrolytes whereas it is 5$\times$ that of the DMC-based electrolyte. At around 1 °C, there is a discontinuity in the conductivity of the DMC electrolyte. This temperature is very close to the freezing point of DMC (Table 2), at which the mobility of the charged species is expected to lower significantly. The conductivity of the DEC-based electrolyte does not exhibit a discontinuity because the melting temperature of pure DEC is much lower (−43 °C). The conductivity of the DMC electrolyte is higher than the DEC electrolyte over most of the temperature range above the melting point of the former. In general, the ionic conductivity of an electrolyte ($\sigma$) is governed by the mobility ($\mu$) and concentration ($C$) of the dissociated ionic species as per Equation (2) (below). Because the dipole moment and dielectric constant of both linear alkyl carbonates ($\approx$2–3) are very similar, the extent of dissociation of Li$^+$ and TFSI$^-$ and resulting concentration of charge-carrier ionic species can be expected to be quite identical.
The mobility [Eq. (3)] is inversely related to the radius of the coordination sphere ($r_i$) and the viscosity of the surrounding liquid. A combination of higher viscosity and a larger coordination sphere resulting from the approximately 1.5 times larger molecular volume of DEC compared to DMC (shown in Table 1) could explain the higher conductivity of the latter electrolyte.

The 2-MeGLN-based electrolyte has the lowest conductivity among the electrolytes tested from -40 to 40 °C. Above this temperature its conductivity is higher than the DEC-based electrolyte, which can be readily linked to its viscosity. The viscosity of the three electrolytes was measured in the temperature range 10 to 80 °C and is shown in Figure 4b. It can be seen that the viscosity of the 2MeGLN-based electrolyte is much higher than all the other electrolytes in the entire temperature range. The viscosity values at two temperatures of interest (25 and 40 °C) are listed in Table 3. At 25 °C, the viscosity of 2MeGLN is about 20.78 MPa s⁻¹, which is more than 10 times higher than those of DEC (1.96 MPa s⁻¹) and DMC (1.31 MPa s⁻¹) electrolytes. The viscosity of 2MeGLN decreases from 42.78 to 4.86 MPa s⁻¹ when the temperature is increased from 10 to 80 °C. The effect of a higher dielectric constant of 2MeGLN may benefit higher dissociation of ionic species but by comparing the temperature dependence of conductivity and viscosity it appears that the conductivity primarily benefits from the large change in viscosity ($\eta_i$) with increasing temperature.

The capacity retention of PAQS was first evaluated in a DOL/DME electrolyte (1:1 by volume) containing 1 m LiTFSI and the obtained results are shown in Figure 5. The cells were initially cycled 20 times at 1 C and 2 C, followed by 1000 cycles at 4 C. After this, the current was reduced to 1 C to compare the capacity retention with the initial 1 C cycles. The capacity for the 2nd cycle was 165.43 mAh g⁻¹, which is about 73% of the theoretical capacity.

### Table 3. Viscosity ($\eta_i$), conductivity ($\sigma_i$), and Walden ($W$) product of four electrolytes (solvent + 1 m LiTFSI) at two different temperatures (25 and 40 °C).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>25 °C</th>
<th>40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_i$ [mS cm⁻¹]</td>
<td>$\eta_i$ [MPa s⁻¹]</td>
</tr>
<tr>
<td>2MeGLN</td>
<td>1.60</td>
<td>20.78</td>
</tr>
<tr>
<td>DOL/DME</td>
<td>24.6</td>
<td>2.10</td>
</tr>
<tr>
<td>DEC</td>
<td>2.46</td>
<td>1.96</td>
</tr>
<tr>
<td>DMC</td>
<td>5.02</td>
<td>1.31</td>
</tr>
<tr>
<td>EC/PC/3DMC</td>
<td>12.76</td>
<td>2.74</td>
</tr>
</tbody>
</table>

Figure 5. Discharge capacity and efficiency of PAQS tested in half cells under the following regime a) 20 cycles at 1 C and 2 C, b) 1000 cycles at 4 C, and c) 20 cycles at 1 C. Electrolyte used is DOL/DME (1:1 by volume) + 1 m LiTFSI.
Theoretical capacity of PAQS (225 mAh g⁻¹). When the current is increased to 2C and 4C, the discharge capacity decreases to 142.56 and 127 mAh g⁻¹, which is only an 8% and 17% reduction, respectively. This indicates that PAQS possesses fast redox kinetics, which is helped also by the small crystallite size (20–40 nm) observed in the TEM images (Figure S5) and good conductivity of (DOL/DME + 1 M LiTFSI) mixture. The capacity fade rate calculated over the course of 1000 cycles is 0.016% per cycle, most of which occurs during the first 200 cycles only. By comparing the discharge capacity at 1C (before and after), a capacity fade rate of 0.003% per cycle is obtained. The efficiency obtained during the entire cycling was above 99.7% as can be seen in Figure 5b. The combination of a high efficiency, low capacity fade, and good high rate capability makes PAQS a suitable electrode material for use in high-performance energy storage devices.

As mentioned previously, the three additional electrolyte solvents selected were 2-MeGLN, DEC, and DMC. The normalized discharge capacity (%) obtained in these electrolytes as a function of the cycle number for the first 50 cycles at 1C current is plotted in Figure 6. The peak discharge capacity obtained on the first 50 cycles for 2-MeGLN and DEC electrolytes was 116 and 103 mAh g⁻¹, respectively, which is much lower than that obtained in DMC (134.103 mAh g⁻¹). It follows the trend DMC > DEC ≈ 2-MeGLN, which is in agreement with the trend in conductivity of the respective electrolytes indicating that the difference in observed capacity may be owed to mass transport limitations. The increase in discharge capacity of 2-MeGLN during the first 7–8 cycles is similar to that observed consistently in the case of the DMC electrolyte, although in this case the effect is more pronounced. Notably, the ability of any electrolyte to swell the PAQS is crucial for the delivery of cations to the redox centers in the electroactive polymer. Moreover, because of the high viscosity (20.78 MPa s⁻¹, 25°C) of the dinitrile electrolyte it is likely that the process of wetting of the PAQS electrode may be much slower than with the alkyl carbonate. The capacity fade rate measured starting from the highest discharge capacity in 2-MeGLN electrolyte is 0.71% per cycle, which is about 3× higher that in the DMC electrolyte (0.26% per cycle). The discharge capacity of PAQS in the DEC electrolyte decreases precipitously after the 30th cycle. This is coincident with a sudden decrease in the in the coulombic efficiency (shown in Figure S3) from approximately 96 to 80% indicating that certain side reactions are prominent (possibly electrolyte degradation at the lithium interface).

For further understanding of the underlying mechanism of the respective capacity fades in the electrolytes, the voltage profiles of the 5th, 15th, 30th, and 50th cycles and corresponding dQ/dV curves for 2MeGLN are shown Figures 7a,b. Similar curves for DEC electrolytes are shown in Figure S8a,b. For the DEC electrolyte, it can be seen from the reduction half of the voltage profile that up to the 15th cycle the end of reduction is reached before the lower voltage limit (1.6 V vs. Li/Li⁺). However, for the 30th and 50th cycle this does not appear to be true because of the large increase in cell impedance during cycling, which forces the reduction plateau to a lower voltage (note lowering of the center potentials shown in Figure S8 from 2.03 V for the 5th cycle to 1.83 V for the 30th cycle).

In the corresponding dQ/dV curve, the same effect can be visualized more clearly, where the reduction peak potential is seen to shift to lower voltages. A similar shift in the opposite direction is observed on the charging peak with the progress of cycling.
of cycling (indicated by green arrows). It is noteworthy that in the case of DEC, unlike any of the other electrolytes, the effect of impedance is equally visible on both during charging and discharging. As this is a two-electrode measurement, it is difficult to accurately comment whether this impedance arises because of some interaction of the electrolyte solvent at the PAQS interface or possibly due to resistive SEI formation owing to electrolyte decomposition at the lithium interface. In conventional electrolytes, the role of EC has been shown to be crucial for stability of the carbonate electrolytes at low potentials, which is absent in this electrolyte.\[^{[29]}\] In the case of 2-MeGLN, the capacity fade trend does not exhibit any sharp discontinuities. The dQ/dV curves indicate a clear two-step oxidation and two-step reduction process (according to Scheme 1), which is not obvious from the galvanostatic voltage profiles. By comparing the height of the peaks and the area under the individual peaks, it is clear that the step I of reduction is kinetically more favored as compared to the step II. In the ideal case, both steps should yield identical capacity of 122.5 mAh g\(^{-1}\) each. However, it appears that not all the monomer units undergoing step I are following up with step II, indicating some structural factor that impedes insertion of the additional cation. During oxidation, it can be seen that: 1) the peak potential of step II shifts to higher potentials (black arrow) and 2) the onset potential for oxidation increases (green arrow). In contrast, the step I peak potential during oxidation is unchanged (indicated by black arrows). It can be envisioned that an anthraquinone redox unit in the polymer chain that has not been able to undergo the step II of the oxidation will not be able to undergo step I as well. Such a component of the polymer may not be able to take part in the following redox cycles and show up as capacity fading of the electrode. Through this reasoning, we propose that the choice of an electrolyte for the PAQS electrode must not only consider the solubility aspect but also take into account the impact on the kinetic aspect and the reversibility of the redox process.

**Effect of composition and nature of the solvent component on the ternary mixture on the electrochemical performance of PAQS**

The most common mixture of solvent used in Li-ion batteries is the ternary system EC/PC/DMC. It is generally chosen and used at the industrial scale because it combines the most sought properties in a solvent for batteries: EC helps in the formation of SEI, PC ensures the temperature resistance, and DMC improves the fluidity of the mixture. Here, we chose EC/PC/DMC mixtures in a ratio by weight of 1:1:3, 1:1:9, and 0:0:1 with 1 M LiTFSI in each mixture. The cells were cycled at 1 C with potential limits of 1.6 and 3.0 V versus Li/Li\(^+\). The first mixture has a composition very similar to electrolytes used in conventional Li-ion batteries, whereas the other two have progressively higher DMC and lower EC + PC content. The discharge capacity (reduction) obtained is plotted as a function of the cycle number in Figure 8.

It can be seen that the EC + PC content of the electrolyte has a pronounced effect on the capacity retention. In the EC/PC/3DMC electrolyte, which contains the highest fraction of EC and PC, the capacity retention is the lowest closely followed by EC/PC/9DMC. The capacity fade rate calculated by linear fitting for the DMC electrolyte (0.26% per cycle) is about 4 \(\times\) better than the EC + PC containing electrolytes (1.06 and 1.08% per cycle, respectively). For both electrolytes containing EC + PC, the maximum capacity loss occurs during the first 10–15 cycles. On the contrary, for the DMC electrolyte, the capacity increases slightly for the first 10 cycles after which it begins to decrease gradually at a constant rate. The average initial discharge capacity following the following order: DMC > EC/PC/9DMC > EC/PC/3DMC, which appears coherent with the observation of a higher solubility of PAQS in (EC + PC)-containing solvent mixtures as shown in Figure 3. This could explain not only why the initial capacity is the highest for PAQS in pure DMC electrolyte, but also why it does not undergo rapid capacity fade in the initial cycles as in the other two electrolytes. The coulombic efficiency for cells with all three electrolytes was > 99.5% over the 50 cycles, which precludes the occurrence of any significant side reactions.

It is interesting to note that increasing the DMC fraction from 60 wt% (EC/PC/3DMC) to 82% (EC/PC/9DMC) has a very small impact on the capacity fade rate implying that the solvents having higher solubilizing power (EC + PC) can preferentially solvate and dissolve the PAQS even if present in lower concentration. In fact, when we consider the solubility of the active material, we must consider it in two forms. The neutral oxidized form, for which we performed the solubility tests, and the reduced form, which is a salt [PAQS]\(^{[2n]}\) [2nLi]\(^{+}\). The latter form is even more likely to be dissolved and dissociated in the presence of polar solvents with high dissociative power for salts such as EC and PC (\(\varepsilon = 80\) and 65, respectively).

In some recent articles, conjugated carbonyl electrodes cycled in organic carbonate electrolytes demonstrated to have very high capacity fade.\[^{[8, 16]}\] Common to all these articles is the use of high EC content in the solvent mixtures, which has traditionally served well in Li-ion batteries. The use of EC is neces-
sary owing to its superior SEI-formation ability on the graphite anode to prevent sustained electrolyte decomposition and its ability to promote salt dissociation for higher ionic conductivity ($\approx 12.5$ mS cm$^{-1}$).\cite{29,30}

However, if using PAQS as an anode that operates well within the stability window of the electrolytes, our results demonstrate that an electrolyte consisting of pure DMC + 1 m LiTFSI has sufficient conductivity (5.02 mS cm$^{-1}$) and offers enhanced capacity retention.

To understand the capacity fade mechanism in further detail, the voltage profiles of the PAQS electrodes were compared for the 1st, 10th, and 50th cycles of the DMC and EC/PC/3DMC electrolyte in Figures 9a,c respectively. The corresponding $dQ/dV$ curves for the shown voltage profiles are plotted in Figures 9b,d for easier visualization of some of the finer differences.

Although not discernible in the voltage profiles, it can be clearly observed from $dQ/dV$ curves for the first cycle that there are two peaks for charging and two peaks for discharging. In the literature, these two peaks corresponding to the two-step redox are more resolved in the case of Na$^+$ or K$^+$ insertion/deinsertion in PAQS.\cite{7,6} As the cycling progresses in the EC/PC/3DMC electrolyte, the oxidation peak corresponding to step II appears to shift to higher potentials. This can be observed in Figure 9c,d, as indicated by the green arrows. The center peak potential from the $dQ/dV$ curve shifts approximately 150 mV from 2.15 to 2.30 V. Over the course of 50 cycles it can be seen that the capacity corresponding to step II is almost completely lost. It is interesting to note that if the capacity fade mechanism in PAQS were driven solely by the dissolution of the electrode material, we would simply expect a diminishing peak size in the $dQ/dV$ curve. However, from these observations, it appears that the oxidation progressively becomes more kinetically hindered with cycling and is also partly responsible for the capacity fade in this electrolyte. It is possible that this may be linked to the dimerization of the anthraquinone anion and its impact on the electrochemical reversibility.\cite{31} It is interesting to note the appearance of a prominent new peak at 2.9 V in Figure 9d with no obvious analogue during reduction. The higher driving force corresponding to the higher potential may be responsible for at least part of the hindered oxidation to occur. On the other hand, during the reduction, the peaks can be seen to become much smaller corresponding to the decrease in capacity but the overall peak potential does not change. At the end of the 50 cycles, the remaining capacity is $\approx 60$ mAh g$^{-1}$, which is quite comparable to only half of the initial capacity indicating that it is only step I of the redox reaction of PAQS that is reversible in the (EC + PC)-containing electrolyte.

In the pure DMC electrolyte, during the first 10 cycles the charge capacity actually increases by about 10 mAh g$^{-1}$, which

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**Figure 9.** Voltage profile vs. capacity of PAQS in a) DMC and c) EC/PC/3DMC electrolyte at a current of 1 C. Corresponding $dQ/dV$ curves for the voltage profiles in b) DMC, and d) EC/PC/3DMC electrolyte (Inset: growth of new peak at high potential). Both electrolytes contain 1 m LiTFSI.
could be related to better wetting of the cathode material by the electrolyte. In the other two electrolytes, a similar effect, if present, may be completely masked by the large capacity fade from the electrode dissolution. An analogous oxidation peak at high potential appears at 2.85 V in this electrolyte although it is not as prominent as in the EC/PC/3DMC electrolyte. Overall, it appears that the presence of the more polar cyclic alkyl carbonates such as EC and PC are more detrimental to the capacity retention in PAQS. To understand the nature of this hindered oxidation we were conducting pulsed field gradient (PFG)-NMR investigations on PAQS electrodes to compare the Li-ion mobility in electrodes, which are cycled in DOL/DME electrolytes and the alkyl carbonate electrolytes. The results of this investigation may be part of a following publication. Thus, it is shown that the low viscosity (0.63 MPas) and low dielectric constant (\(\varepsilon = 3.1\)) member of the organic carbonate group is a more suitable electrolyte solvent from a PAQS capacity retention point of view.

Conclusions

Polyanthraquinone sulfide (PAQS) was successfully synthesized by the polycondensation method (Phillips process) and the phase purity of the obtained material was confirmed by FTIR and Raman spectroscopy. Because the solubility of organic electrode materials is known to be a primary roadblock in attaining good capacity retention, we conducted a comprehensive study to understand its general solubility characteristics across 17 different solvents. The solubility of PAQS spans a wide range from almost complete insolubility in water to very high solubility in DMF and DMSO. The solubility in \(\gamma\)-butyrolactone (ester) was sufficiently high to rule out the use of this solvent as an electrolyte for PAQS. In general, the low dielectric constant linear alkyl carbonates (DEC, DMC, EMC) have a much lower solubilizing power compared to the high dielectric constant cyclic carbonates (EC, PC). The general trend of solubility could be predicted with good accuracy using the Hansen solubility parameters analysis. Physical characterization of the electrolytes containing 1 \(\text{m} \text{LiTFSI}\) reveals the following order of conductivity ethers > alkyl carbonates > dinitriles. The extremely high viscosity of the dinitrile at and below room temperature are responsible for its low conductivity, which increases rapidly as the temperature is increased beyond 45 °C. The low capacity retention of PAQS in alkyl-carbonate-based electrolytes reported previously is shown to be linked directly to the presence of cyclic alkyl carbonates, which not only lead to the rapid dissolution of PAQS but are also responsible for the irreversibility of step II of the redox process. In an electrolyte composed of only DMC, the capacity fade rate is about 4 x lower than in the presence of EC + PC. In the dinitrile electrolyte, the effect of dissolution is less prominent compared cyclic alkyl carbonates, however the problem of irreversibility of the second step of reduction is clearly observed. Overall, it has been shown that although the problem of PAQS solubility is of great significance for the capacity retention and must dictate the electrolyte solvent selection, it is equally important to consider the kinetic aspect and the reversibility of the redox reaction, which is also intricately linked to the solvent used in the electrolyte.

Experimental Section

PAQS was prepared by refluxing a solution of DCAQ with Na,S in NMP at 200 °C according to methods described previously.\(^{[7,16]}\) The reaction mixture was maintained at the aforementioned temperature for 10 h with constant magnetic stirring. It was then allowed to cool down to room temperature and the polymer was obtained by vacuum filtration and washed with water several times to remove any unreacted Na,S. The filtered polymer was then dried at 60 °C under vacuum for 12 h after which a dark brown colored powder was obtained.

To prepare the electrodes, the appropriate quantity of PAQS was mixed with conductive carbon (C65, Timcal) in a mortar and pestle. To this mixture, a 5 wt-% solution of polyvinylidene fluoride (PVDF) in NMP was added to obtain a final ratio of 4:5:1 (by weight) of PAQS/C65/PVDF. The obtained slurry was painted on conductive carbon paper (GDL 28 BC, SGL Group) to prepare the electrodes, which were then dried at 90 °C under vacuum for 1 h to remove the NMP. A typical electrode had an active material loading of about 2 mg cm\(^{-2}\). For electrochemical testing, the PAQS electrodes were assembled in half cells with a Li foil counter electrode and the appropriate electrolyte. Two sheets of Whatmann glass fiber separator (GF/C) were placed between the electrodes in CR2032 coin cells. The entire cell assembly process was performed inside a glovebox in which the moisture and oxygen level was < 0.1 ppm. Electrochemical characterization was performed on a Biologic instrument and 225 mAh g\(^{-1}\) was assumed as the theoretical capacity for calculating the current.

Conductivity measurements were performed using a Multichannel Conductivity Meter (BioLogic, France) based on frequency Response Analyser (MCM 10) connected to a Peltier-based temperature control unit (WTSH 10). The measurements were made from 80 to −40 °C using Pt parallel plate electrodes using sealed cells protecting the samples from air exposure. The viscosity measurements were performed between 5 and 80 °C using and Anton Parr digital rolling ball viscometer. The temperature of the cell during measurement was controlled within ±0.02 °C.

For UV/Vis spectroscopy measurements, PAQS (50 mg) was added to the electrolyte solvents (5 mL) in which the solubility was to be tested. The glass vial containing the mixture was kept in a temperature-controlled oven at 40 °C for 48 h to allow the PAQS to reach the equilibrium dissolved concentration at this temperature. The undissolved PAQS remained at the bottom of the vial while a yellow colored supernatant was removed carefully (avoiding any undissolved particles) with a syringe for UV/Vis spectroscopy. The measurements were performed on a spectrophotometer (Jasco V-670) in the wavelength range of 350–700 nm.

Acknowledgements

The authors would like to thank “Le Studium Loire Valley Institute for Advanced Studies” for financial support to researchers involved in this study.
Conflict of interest

The authors declare no conflict of interest.

Keywords: Hansen parameters · organic batteries · organic electrode · polyanthraquinone · solubility


Manuscript received: October 15, 2017
Revised manuscript received: November 17, 2017
Accepted manuscript online: December 5, 2017
Version of record online: February 15, 2018