Exploring Eutectic Mixing of Quinones for Engineering High Energy-Density Electrolytes

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Abstract

Eutectic electrolytes can attain high concentrations of redox-active species, offering a path toward high energy density redox flow batteries. Here we introduce a new entropically-driven eutectic mixing approach using organic small molecules. By mixing chemically similar redox-active species, we engineer highly concentrated, low viscosity liquids composed almost entirely of redox active molecules. Using quinones as a model system, we discover a ternary benzoquinone eutectic mixture and a binary naphthoquinone eutectic mixture which have theoretical redox-active electron concentrations of 16.8 and 8.8 M e−, respectively. We investigate compatibility with protic supporting electrolytes and quantify ionic conductivity and viscosity of quinone eutectic electrolytes across multiple states of charge. A binary naphthoquinone eutectic electrolyte with a protic ionic liquid supporting electrolyte (7.1 M e−, theoretical volumetric capacity 188 Ah L−1) achieves a volumetric capacity of 49 Ah L−1 in symmetric static cell cycling. These preliminary results suggest that entropy-driven eutectic mixing is a promising strategy for developing high energy density flow battery electrolytes.
Introduction

Redox flow batteries, which store energy in liquid electrolytes, are an attractive technology for grid energy storage due to advantages including favorable scalability, decoupled power and energy, and flexible design.¹ These liquid electrolytes, known as the posolyte and negolyte, are typically composed of dilute redox-active species and supporting salt dissolved in a redox-inactive solvent.²⁻⁴ To date, aqueous chemistries with inorganic redox species, especially vanadium, are the most technologically developed.⁵ Two key challenges remaining for redox flow batteries are low energy density and power density, both of which result from low cell voltages and low concentrations of redox-active species in the electrolyte. Though not generally considered a constraint for grid storage technologies, improving energy density can reduce capital and balance-of-system costs, which will become increasingly important to overall costs as flow battery systems reach maturity.⁶,⁷ Though many chemistries have been explored, both aqueous and non-aqueous chemistries face challenges in reaching high energy density. Aqueous chemistries are limited by the electrochemical stability window of water, and though stable in a larger voltage window, non-aqueous chemistries face high costs for solvents and supporting salts.⁴,⁷⁻⁹ Furthermore, both chemistries struggle to reach high concentrations due to limited solubility of the redox-active species.¹⁰,¹¹

Various strategies have been used to increase the redox-active concentration in flow battery electrolytes and obtain higher energy density. Molecular engineering has been widely applied to organic redox-active species, with functional groups added to increase solubility¹²⁻¹⁴ or depress the melting point.¹⁵⁻¹⁷ To evade solubility limits altogether, semi-solid slurry electrolytes¹⁸ and redox targeting¹⁹ have been developed, using solid redox materials in addition to the dissolved redox active species to reach higher concentrations. Still, these strategies face challenges, most notably the high viscosity of the resulting electrolytes, which demands increased pumping power and results in slower mass transport, including decreased ionic conductivity and active species diffusivity.²⁰ To address these issues, here we demonstrate a new approach using entropy-driven eutectic mixing to develop energy-dense
electrolytes with both high concentration and low viscosity.

**Eutectic Electrolytes in Flow Batteries**

The liquid electrolyte in a flow battery is conventionally framed as a set of solutes (including the redox active species and supporting salt) dissolved in a solvent (Fig. 1a-b). The solvent, be it water or an organic solvent, is liquid at the temperatures of operation, and the solubility limit of the solutes in a given solvent governs the highest concentration of the solutes (Fig. 1e). Thinking more broadly, the liquid electrolyte can instead be considered as a eutectic system which is liquid within certain boundaries of temperature and composition. Notably, this system does not necessarily include any component that, by itself, is liquid at these temperatures, i.e. a solvent (Fig. 1c-d). Briefly defined, in a eutectic system the melting point of the mixture is lower than the melting point of any individual component (Fig. 1f), with the decrease in melting point driven by an increase in entropy (and in many cases, including deep eutectic solvents (DESs), a decrease in enthalpy) upon mixing. Here we refer to “eutectic mixing” as the strategy of decreasing melting points by mixing, even if the mixture does not lie exactly on the eutectic composition, which has the lowest melting point.

Fundamentally, the solvent-led approach and the eutectic mixing approach are both subject to the same chemistry and physics of mixtures. However, they represent different strategies for liquid electrolyte design. The eutectic mixing approach has two potential benefits. First, by avoiding use of solvent, higher energy densities in liquid electrolytes can be achieved. Second, by avoiding solvents such as water, which have limited electrochemical stability windows, the accessible voltage range may be increased. Further, because the eutectic mixing approach may examine compositions not typically accessible with the solvent-led approach, it presents the opportunity to discover new electrolytes.

For both approaches, the electrolyte must remain liquid at all states of charge despite
Figure 1: Strategies to design liquid electrolytes for flow batteries. (a-b) Solvent-led approaches. These include the use of low-melting point solvents, such as water or nonaqueous solvents (a), or deep eutectic solvents (DESs) (b). (c-d) Eutectic approaches. These include enthalpy-driven approaches using redox-inactive, eutectic-forming additives (c), and entropy-driven approaches using only redox-active molecules (d), which can yield the highest theoretical energy density. (e-f) Schematic phase diagram of the solvent approach (e), whereby the liquid contains a large molar fraction of redox-inactive species, and the entropy-driven eutectic mixing approach (f), which achieves a liquid composition by mixing redox-active species without additional solvent or redox-inactive additives.

The changing composition of the mixture as species are oxidized or reduced during charge and discharge. This remains a challenge for high-energy-density liquid electrolytes due to differences in solubility, melting point, or eutectic behavior of active species in their oxidized and reduced states.\textsuperscript{24,25}

To date, studies on eutectic electrolytes have predominantly taken an enthalpy-driven approach focused on selecting components with favorable intermolecular interactions including hydrogen bonding, Lewis acid-base interactions, and other intermolecular forces.\textsuperscript{21} This strategy employs two or more species, one of which is usually redox-inactive and therefore decreases the energy density of the system. Examples include metal-based eutectics,\textsuperscript{26–28} formed by mixing redox-active metal halides with quaternary ammonium salts and/or hydrogen bond donors, and organic-based eutectics,\textsuperscript{25} formed via interactions between functional groups on the redox-active species and alkali metal fluorinated sulfonylimide salts. In
some cases these mixtures result in organic eutectic electrolytes with concentrations up to 3.7 M.\textsuperscript{22,25} However, this approach is limited by its requirement for high molar fractions of redox-inactive salt. Additionally, the functional group which coordinates to form the eutectic is often also the redox active site. This prohibits formation of the eutectic (and thus the liquid electrolyte) across multiple states of charge, making it impossible to form an electrolyte which remains liquid upon both charge and discharge.\textsuperscript{25} The enthalpic strategy has also been applied to form a mixed-electrolyte in which the posolyte and negolyte redox-active species are each a eutectic component,\textsuperscript{29} without the inclusion of additional redox-inactive eutectic components. Though the total concentration reached 3.5 M, the mixed-electrolyte approach effectively dilutes each component by a factor of two, limiting the maximum concentration that can be achieved. Redox-inactive deep eutectic solvents have also been investigated.\textsuperscript{30–32} In these systems the redox-active species is not a eutectic component, resulting in similar limitations to other solvent-led approaches, including low solubility of redox active species and high viscosity.\textsuperscript{33}

Our approach, which theoretically could achieve the highest energy density of the above approaches, uses eutectic mixing to lower the melting points of mixtures composed entirely of redox-active components. If these compounds have similar molecular structures, then the change in enthalpy upon mixing will likely be small, and a decrease in the melting point will be driven by the entropy of mixing, which increases with the number of distinct components in the mixture.\textsuperscript{34} We demonstrate this approach using mixtures of quinones as a model species. We select quinones, which are widely applied in aqueous flow battery chemistries,\textsuperscript{2,35–37} because their low molecular weight and well-known ability to undergo reversible 2-electron redox make them attractive candidates for a high energy density eutectic electrolyte.\textsuperscript{38} Additionally, many quinone derivatives are commercially available, providing a range of chemically similar compounds to study.

In this work we outline how the entropy-driven eutectic mixing approach can be used for electrolyte engineering and examine the performance and opportunity of eutectic quinone
electrolytes. First we demonstrate the use of eutectic mixing to depress quinone melting points for oxidized and reduced species, and mixtures thereof, resulting in highly concentrated quinone eutectics which are liquid across the entire state of charge (SOC) range. With promising mixtures identified, we investigate compatible supporting electrolytes to introduce ionic conductivity in these systems, and quantify properties (concentration, viscosity, and ionic conductivity) relevant to flow batteries. Finally, we evaluate the preliminary electrochemical performance of a quinone eutectic electrolyte via symmetric-cell cycling.

To show the generalizability of this approach we investigate the properties of multicomponent eutectic electrolytes for two different classes of quinone molecules, 1,4-benzoquinone derivatives and 1,4-naphthoquinone derivatives, and their reduced protonated (hydroquinone) counterparts. While we focus on quinones in this work, entropy-driven eutectic mixing is a general approach which could be applied to other redox-active species to form new highly-concentrated electrolytes.

Results and Discussion

Eutectic Liquid Quinones

Melting Properties of Quinone Eutectics

Using the entropy-driven eutectic approach, we engineer the mixture to be in a liquid state by tuning the molecular composition. To obtain a quinone electrolyte that is liquid at all states of charge, this requires eutectic melting point depression for oxidized quinones, the corresponding reduced quinone species, and all mixtures of the two. To discover which mixtures of quinones are promising, we begin by identifying the melting points of the redox-active quinone components in their oxidized and reduced forms.

We investigate the melting properties of oxidized quinones using a subset of benzoquinone, naphthoquinone, and anthraquinone species with varying side groups. Using differential
scanning calorimetry (DSC) we measure oxidized quinone melting points for both individual quinones and mixtures, as shown in Fig. 2a. Pure component melting points range from 31-289 °C, and the wide range is expected due to the dependence of melting point upon the identity and number of substituent groups. Though quinone species in this study have melting points as low as 31 °C, the melting point of the reduced quinone is not necessarily as low. This motivates eutectic mixing to depress the melting points of all components in all states of charge. Our prior work showed that differently substituted 1,4-benzoquinones can be combined to form a eutectic mixture with a lowered melting point.\textsuperscript{34} In general, we observe that melting point depression increases with the number of components in the mixture, with melting points as low as -6 °C recorded for an equimolar mixture of 7 components (Fig. 2a). Here we find that the entropy-driven eutectic mixing approach successfully depresses the melting point of benzoquinones, naphthoquinones and anthraquinones, showing the generalizability of this strategy (Fig. 2b). In contrast, enthalpy-driven eutectic mixing strategies that depend on intermolecular interaction have not been successful for naphthoquinones due to steric effects.\textsuperscript{25} DSC data can be found in the Supporting Information (SI Fig. S1, S3, S4).

Reduced quinones tend to have more polar bonds than oxidized quinones, leading to stronger intermolecular reactions and thus higher melting points.\textsuperscript{39} This makes it more challenging to achieve a low melting point eutectic for the reduced quinone mixture, as reflected by the results in Fig. 2a. The identity of the reduced species depends strongly on the pH conditions and supporting cation.\textsuperscript{38,40} As a result, changing the supporting electrolyte or working cation (\(H^+\), \(Li^+\), \(Na^+\)) of the quinone battery system results in reduced quinone species with different properties.

To maximize energy density, it would be ideal to pair a quinone posolyte with an alkali metal negolyte, such as Na-K or Li, which would result in a high-voltage system (> 2.5 V). We investigated the reduced species of hypothetical liquid quinone-alkali metal batteries by chemically synthesizing quinone-alkali metal compounds with Li, Na, and K. However, we
found that the quinone-alkali metal compounds were high sensitivity to air and water, and observed that they undergo a decomposition reaction prior to melting. Due to the inability to form liquid reduced species without decomposition at experimentally relevant temperatures, we did not investigate this path further. Additional details regarding the synthesis and testing of these materials can be found in the Supporting Information.

In contrast, we find that reduced quinones paired with protons, known as hydroquinones, have lower melting points than the quinone-alkali-metal compounds and can form eutectics at lower temperatures and without undergoing decomposition (Fig. S2). For the hydroquinone forms of the compounds studied here, we measure melting points from 76-239 °C for single components via DSC (Fig. 2a). We observe eutectic melting point depression for mixtures of hydroquinones, and, like the oxidized form, the melting point can be further decreased by increasing the number of components (Fig. 2a). This again is in contrast to enthalpy-driven eutectic mixing strategies with sulfonylimide salts, which work for quinones but have not been successful for hydroquinones due to differences in intermolecular interactions (and thus, enthalpy of mixing) for the ketone versus hydroxyl functional groups.\(^{25}\)

Although a large number of components would decrease the melting point further (theoretically arbitrarily low, given enough components),\(^{34}\) here we focus on a ternary benzoquinone mixture and a binary naphthoquinone mixture as a proof of concept. To select the mixture components, we favor molecules with low melting points and low molecular weights, which tend to be correlated (following the general trend benzoquinones < naphthoquinones < anthraquinones) (Fig. 2b). Also following this trend, we observe higher concentrations and lower viscosities for smaller molecules (Fig. 3), which are both desirable properties for a flow battery electrolyte.

Based on these design rules, we identify an equimolar mixture of 2-methyl-1,4-benzoquinone (Q2), 2-chloro-1,4-benzoquinone (Q4), and 2-tert butyl-1,4-benzoquinone (Q5) as our ternary benzoquinone eutectic (BQE) system. This mixture demonstrates the high energy density that can be achieved by mixing low molecular weight compounds (average MW = 142.95
Figure 2: Melting temperatures of quinone molecules. (a) Eutectic melting points of single, binary, ternary, and multi-component (4+) mixtures of quinone species in the quinone (oxidized) and hydroquinone (reduced) forms. Melting points include experimental values from this work and values from literature (See SI Table 2 for values and references). (b) Molecular weight versus quinone melting point for selected benzoquinone, naphthoquinone, and anthraquinone species and corresponding equimolar eutectic mixtures of each. The BQE and NQE mixtures are labeled.

g mol$^{-1}$. We also identify a binary naphthoquinone eutectic (NQE) system composed of 2,3-diethyl-1,4,naphthoquinone (DENQ) and 2,3-diisopropyl-1,4,naphthoquinone (DIPNQ) in an equimolar mixture. Though the naphthoquinones have higher melting points and molecular weights than the benzoquinones, they are fully-substituted and have improved chemical stability, as discussed in a later section. Properties of the mixtures of interest are reported in Table 1. Melting points for the individual quinones and both the BQE and NQE mixture are plotted in Figure 2b, and data for additional eutectic quinone mixtures can be found in SI Table 2.
Table 1: Properties of eutectic quinone mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Quinone Species</th>
<th>Avg MW</th>
<th>$M_e$</th>
<th>$T_{m,ox}$</th>
<th>$\Delta T_{m,ox}$</th>
<th>$T_{m,red}$</th>
<th>$\Delta T_{m,red}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BQE</td>
<td>2-methyl-1,4-benzoquinone</td>
<td>142.95</td>
<td>16.8</td>
<td>42.2</td>
<td>13.3</td>
<td>60.9</td>
<td>50.8</td>
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<tr>
<td></td>
<td>2-chloro-1,4-benzoquinone</td>
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<tr>
<td></td>
<td>2-tertbutyl-1,4-benzoquinone</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NQE</td>
<td>2,3-diethyl-1,4,naphthoquinone</td>
<td>228.29</td>
<td>8.8</td>
<td>40.0</td>
<td>28.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,3-diisopropyl-1,4,naphthoquinone</td>
<td></td>
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Average molecular weight, redox-active electron concentration ($M_e$), and melting points for quinone eutectic mixtures of interest. $T_{m,ox}$ and $T_{m,red}$ are the mixture melting points in the oxidized (quinone) and reduced (hydroquinone) forms, respectively. $\Delta T_{m,ox}$ and $\Delta T_{m,red}$ are the average melting point depression for species in each mixture. All temperatures are reported in °C.

For DENQ, $T_{m,red}=144.0$ °C. We were unable to measure the melting properties of the hydroquinone forms of DIPNQ or the NQE mixture due to limited yields from chemical synthesis, thus $T_{m,red}$ and $\Delta T_{m,red}$ for the NQE mixture are not reported.

**Redox-Active Concentration**

The resulting quinone eutectics are highly concentrated redox-active liquids. We calculate the redox-active electron (RAE) concentration of the liquid quinones assuming a 2 electron redox capacity per molecule. Under this assumption, the BQE has a 16.8 M RAE concentration and the NQE has 8.8 M RAE, with the lower concentration of the NQE due to the higher molecular weight of the naphthoquinones, which contain an additional phenyl ring (Table 1). Comparing the NQE to other liquid naphthoquinones in literature, which use bulky side groups to depress melting point or increase solubility, further exemplifies this relationship between molecular weight and RAE concentration. With only short alkyl sidechains, the NQE reaches a 46% greater RAE concentration than a glycolated liquid naphthoquinone reported by Shimizu et al. as shown in Fig. 3, which achieves melting point depression due to its long diethylene glycol monomethyl side chains. The BQE and NQE concentrations also greatly exceed those attained for quinones or other organic species via a solvent-led approach, which are typically less than 1.5 M RAE.

**Mixture Viscosity**

Low electrolyte viscosity is required to minimize to pumping power and ohmic losses in flow batteries, with <10 mPa·s suggested in the literature as an upper limit for a practi-
Figure 3: Viscosity versus redox-active electron concentration for liquid quinones. Data include eutectic quinone electrolytes (this work, filled circles), in the gray highlighted region, and data from literature (open circles) for comparison to solvent-led and molecular engineering approaches. (a) Liquid quinones, including this work (NQE, BQE) and a glycolated naphthoquinone liquid via molecular engineering. $\text{15}$ -Q and -HQ indicate the quinone and hydroquinone forms of the mixture, respectively, while -Q/HQ is a 1:1 mixture of the quinone and hydroquinone forms. Inset (b) highlights the low viscosity of single-component benzoquinones and the BQE mixture in the BQE-Q and BQE-Q/HQ compositions. (c) Liquid quinones with supporting electrolyte. For the eutectic quinone mixtures, NQE-Q:PIL indicates the oxidized form of the NQE mixed with an imidazole-imidazoliumTFSI NSPIL in a 5:1 ratio (NQE-Q:PIL). BQE-Q:AA/W indicates a mixture of the BQE mixture with acetic acid and water in a 10:5:1 molar ratio (BQE:AA:W). We show a comparison to the molecular engineering approach, with a glycolated liquid naphthoquinone with LiTFSI in a 5:1 molar ratio, $\text{15}$ and to the solvent-led approach, with a vanadium electrolyte $V_2(\text{SO}_4)_5$ with 5 M total sulfates concentration. $\text{43}$
To assess the practicality of eutectic quinones, we measure the viscosity of quinone single components and eutectic mixtures (Fig. 3a). Fig. 3b highlights the low viscosities observed for highly concentrated benzoquinone eutectics, including the BQE, a binary quinone mixture, and three single-component quinone liquids (values tabulated in SI Table 3). Depending on the melting points of individual compounds and mixtures, viscosities as low as 1.5 mPa·s can be reached at 35 °C, such as for a mixture of 2-methyl-1,4-benzoquinone and 2-isopropyl-5-methyl-1,4-benzoquinone. Like melting point, quinone viscosity also depends on SOC. The reduced (hydroquinone) mixtures exhibit higher viscosities due to stronger intermolecular interactions between the reduced-protonated species. The viscosity of the NQE mixture is 12.8 mPa·s, at 60 °C, notably higher than for the smaller benzoquinone molecules, as expected due to the increased molecular weight. This trend can also be observed by comparison with the glycolated naphthoquinone reported by Shimizu, shown in Fig. 3c, or by comparison to other quinones with long side chains which form highly viscous liquids.

Importantly, the eutectic mixing approach and the solvent-led approach offer distinct ways to tune the redox-active concentration, with differing effects on viscosity. With the solvent-led approach, one might increase the redox-active species concentration by dissolving more molecules or adding side chains to enhance the solubility of a particular species, increasing the viscosity in the process. In the entropy-driven eutectic approach, one would increase the concentration by tuning the mixture composition, selecting redox-active molecules with lower molecular weights (Fig. 3c). As a result, one can simultaneously increase the redox-active species concentration and decrease the viscosity through the engineering of the eutectic components. This offers a path towards highly concentrated electrolytes with practical liquid properties.
Quinone Electrolyte Mixtures: Eutectic Liquid Quinone + Supporting Electrolyte

Reactivity and Ionic Conductivity

A practical electrolyte also requires high diffusivity of ionic species to limit ohmic losses and achieve high power density during operation. We probe this property by measuring ionic conductivity. For the liquid quinones studied here, we measure negligible intrinsic ionic conductivity for the oxidized quinone species. Though the hydroquinone species have non-zero intrinsic ionic conductivity, we find that the addition of a compatible protic supporting electrolyte is necessary to ensure ionic conductivity in the electrolyte at all states of charge. Due to the chemical reactivity of quinones, we screen for compatible supporting electrolytes by heating quinone-supporting electrolyte mixtures at 65 °C for 12+ hours and observing chemical changes with nuclear magnetic resonance spectroscopy (NMR). Here we focus on aqueous acids and protic ionic liquid supporting electrolytes. Description of additional supporting electrolytes tested, including alkali metal salts, can be found in the Supporting Information.

Aqueous Acids  Screening aqueous acids as protic supporting electrolytes uncovers challenges for both the BQE and NQE mixtures. Benzoquinones are known to be highly reactive and undergo a number of chemical reactions including Michael Addition\textsuperscript{2,45} and oligomerization with acidic\textsuperscript{46} or cationic\textsuperscript{47} catalysts. While it has been shown that tri- or tetrasubstituted quinones have increased stability against these attacks,\textsuperscript{48} the benzoquinones in the ternary BQE are monosubstituted, selected for their low melting points in both the oxidized and reduced-protonated forms. As a result, they are vulnerable to chemical reactions at unsubstituted sites on the ring. Indeed, with strong acids and alcohols as supporting electrolytes we observe polymerization of benzoquinone species, evidenced by increased viscosity and darkening of the sample, and by peak broadening in the NMR spectra (SI Fig. S8). The naphthoquinones studied here (DENQ, DIPNQ) are fully substituted and thus more stable to chemical degradation by addition or oligomerization by strong acids. However, they are
found to be immiscible with aqueous acids, thus a different supporting electrolyte is required. (SI Fig. S9, S10)

We also screen the reactivity of weak acids, and find that mixtures of BQE with glacial acetic acid do not result in polymerization. With NMR we observe less reactivity for the BQE species with acetic acid than for the strong acids tested (SI Fig. S13, S12). We further study the properties of a benzoquinone eutectic electrolyte composed of BQE, acetic acid, and water in a 10:5:1 molar ratio. The inclusion of a small amount of water increases ionic conductivity, especially for the reduced, hydroquinone mixture (SI Fig. S5). Notably, the water added is only 6 mol% of the mixture, differentiating this from the major use of solvent occurring in the solvent-led approach. As a result, the energy density remains high, with a RAE concentration of 13.6 M for the BQE:AA/Water mixture (Fig. 3).

For BQE:AA/Water electrolytes chemically prepared at different states of charge, we find that conductivity varies with SOC due to differences in intrinsic ionic conductivity and viscosity (Fig. 4b-c) of the reduced and oxidized quinone species. The highest conductivity, 14 $\mu S \text{cm}^{-1}$ at 85 °C (Fig. 4c), is observed at 50% SOC, due to the combination of higher conductivity for hydroquinone mixtures and lower viscosity for oxidized benzoquinones. However, this ionic conductivity is 3 to 4 orders of magnitude lower than typical values for aqueous and non-aqueous chemistries.\textsuperscript{4,49}

**Protic Ionic Liquids** We investigate non-stoichiometric protic ionic liquids (NSPILs) as anhydrous protic electrolytes. These Brønsted acid-base ionic liquids consist of an organic base, its conjugate acid, and a counter-ion.\textsuperscript{50} NSPILs have low melting points and are ideal for proton-coupled reactions due to the availability of both proton donors and acceptors.\textsuperscript{51–54} NSPILs are prepared at 50% protonation from amines of varying basicity, with bis(trifluoromethane)sulfonimide as the source of protons and TFSI$^-$ counter anions. Though most benzoquinone-NSPIL mixtures studied here are found to react (SI Fig. S12), the naphthoquinone species appear stable to the NSPILs and we observe no evidence of
Figure 4: (a) Ionic Conductivity of eutectic quinone supporting electrolyte mixtures. Ionic conductivity of the BQE with an acetic acid and water supporting electrolyte (10:5:1 BQE:AA:Water) is measured across 3 states of charge, with BQE-Q, -Q/HQ, and -HQ indicating the quinone, 1:1 quinone:hydroquinone, and hydroquinone forms of the mixture, respectively. Mixtures with acetic acid supporting electrolyte have lower ionic conductivity than those with NSPIL electrolytes, as shown by comparison with BQE-Q:PIL (TEA), with triethylamine-triethylammonium (TEA) TFSI NSPIL supporting electrolyte in a 5:1 BQE:PIL ratio, and NQE-Q:PIL (Im), with imidazole-imidazolium TFSI NSPIL supporting electrolyte in a 5:1 NQE:PIL ratio. (b-c) Change in BQE mixture properties with state of charge. The BQE viscosity is minimized in the oxidized, quinone-rich composition (b), while the highest ionic conductivity is measured for the 1:1 Q/HQ mixture (c). All values in (b) and (c) are for measurements conducted at 85 °C with the exception of BQE-Q viscosity, which was measured at 60 °C.

We test NQE:NSPIL mixtures in a 5:1 molar ratio and find that the imidazole-imidazolium TFSI (Im-ImTFSI) NSPIL results in the highest conductivity (SI Fig. S6), with 1.6 mS cm⁻¹ for a NQE:PIL (Im) mixture at 85 °C. With the addition of the redox-inactive NSPIL, the NQE:PIL (Im) (5:1) has a RAE concentration of 7.1 M (Fig. 3), still exceeding concentrations achieved for solvent-led approaches, which also face decreasing energy density at high...
supporting salt concentrations due to diminishing solubility of redox-active species.\textsuperscript{4,36}

In general, we observe higher ionic conductivity for quinone eutectic electrolytes containing NSPIL electrolytes than for those with aqueous acid supporting electrolytes. Comparing BQE-supporting electrolyte mixtures, the conductivity of a BQE-Q:PIL (TEA) mixture (5:1 molar ratio of BQE-Q to triethylamine-triethylammonium TFSI) is 3 orders of magnitude higher than that of a BQE-Q:AA/Water mixture (Fig. 4). The BQE-Q:PIL (TEA) mixture, which reaches a conductivity comparable with solvent-based non-aqueous flow battery electrolytes,\textsuperscript{4,9,49} also has higher conductivity than the NQE-Q:PIL (Im) mixture at all temperatures. This is likely due to lower viscosity of the BQE compared to the NQE.

**Mixture Viscosity**

Addition of supporting electrolyte changes the viscosity of both benzoquinone and naphthoquinone eutectic mixtures. For the BQE, the addition of acetic acid and water decreases the overall viscosity. This is most evident for the hydroquinone form, BQE-HQ:AA/Water, which has a viscosity 74% lower than the neat BQE-HQ without added supporting electrolyte. While BQE-HQ:AA/Water, at 12 mPa·s at 85 °C, is the most viscous state of charge observed for the BQE:AA/Water mixtures, it is much closer to a practical electrolyte viscosity than in the case without supporting salt. For the NQE, the viscosity increases with the addition of the NSPIL. At 60 °C, the viscosity increases from 12.8 mPa·s for the neat NQE to 23.7 mPa·s for the NQE-Q:PIL (Im) mixture (Fig. 3). This is due to contributions from the Im-ImTFSI NSPIL viscosity, 18.5 mPa·s at 60 °C, which is higher than the viscosity of the neat NQE.

**Electrochemical Properties**

Next, we probe the electrochemical properties of eutectic quinone electrolytes, focusing on NQE mixtures due to their superior chemical stability. We perform cyclic voltammetry (CV) of DENQ and DIPNQ diluted in acetonitrile (ACN) solvent with 0.1 M Im-ImTFSI NSPIL
supporting electrolyte. CV of DENQ and DIPNQ at 10 mM concentration reveals a single pair of redox peaks for each species, shown in Figure 5. This feature corresponds to the $2e^-, 2H^+$ reduction of the quinone (oxidized state) to the hydroquinone (reduced state).55–57

The redox features for DENQ and DIPNQ occur in close proximity, with $E_{1/2}$ values equal to -573 mV and -619 mV vs $Fc/Fc^+$, respectively. The large peak splitting, characteristic of a kinetically slow redox process, has been reported for benzoquinones in similar electrolyte environments due to slow proton transfer from the protonated NSPIL cations.38

While here we focus on Im-ImTFSI supporting electrolyte, we note that the selection of organic base in the NSPIL supporting electrolyte presents further opportunities to tune the electrochemistry of the quinone system. By selecting organic bases with varying pKas, one can tune the redox potential of the quinone molecules, characteristic of a proton-coupled electron transfer.56 Differences in redox kinetics and ionic conductivity are also observed (SI Fig. S26a)

Figure 5: Cyclic Voltammetry of DENQ and DIPNQ (10 mM) in ACN with 0.1M Im-ImTFSI NSPIL supporting electrolyte at a scan rate of 50 mV s$^{-1}$.
Static Cell Cycling

Next, we assess the cycling performance of the NQE:PIL (Im) electrolyte using a low-volume static cell in a symmetric configuration. Though the electrolyte is designed for flow battery applications, the large volume necessary for flow experiments, combined with the high volumetric capacity of the electrolyte, poses an experimental challenge due to the long times required to cycle the cell. As such, a simplified setup is used for proof of concept. Experiments are conducted between 60 and 90°C due to the melting points of the eutectic electrolytes of interest.

Membrane Compatibility

The symmetric electrolytes are separated by a modified Nafion 212 proton exchange membrane. Though not optimized for non-aqueous applications, Nafion is employed due to its commercial availability, proton conductivity, and low rates of quinone crossover. In contact with BQE:AA/Water, we observe that the initially colorless Nafion membrane darkens over time (SI Fig. S20). This is consistent with literature, where Nafion is reported to bind to quinones via the nucleophilic sulfonate group on the Nafion polymer, again presenting a challenge due to the chemical reactivity of the benzoquinones studied here. For the NQE:PIL (Im) electrolyte, we observe high impedance when using an aqueous-acid saturated membrane, likely resulting from the immiscibility of the NQE with aqueous solutions. To avoid this issue, we dope the Nafion 212 membrane with the ionic liquid cation by saturation in the NSPIL of choice, Im-ImTFSI, for anhydrous cation conductivity through the membrane.

Cycling Performance

The NQE static cell is prepared at 50% SOC by mixing equimolar quantities of the oxidized (quinone) and reduced (hydroquinone) forms of each active species to form a NQE-Q/HQ:PIL (Im) electrolyte, maintaining the 5:1 molar ratio of NQE:PIL. As such, reported cycling data begins at cycle 0, during which the cell is charged from 50 to 100% SOC. Due to the initial
SOC, the volumetric capacity for cycle 0 charge is normalized to half the electrolyte volume, and coulombic efficiency is not reported. The volumetric capacity for cycle 0 discharge, and all subsequent charge and discharge cycles, is normalized to the total electrolyte volume (Fig. 6). Cycled at 0.2 mA $cm^{-2}$ and 90 °C, the NQE cell achieves a volumetric capacity of 95 Ah $L^{-1}$ on charge 0, from 50 % to 100 % SOC. On discharge 0, 49 Ah $L^{-1}$ is recovered. For subsequent cycles, we observe coulombic efficiency greater than 90% (Fig. 6).

These initial results exceed the 46 Ah $L^{-1}$ theoretical volumetric capacity one can expect from a 1.7 M RAE electrolyte, a typical concentration of a vanadium redox flow battery electrolyte, but much of the quinone capacity still remains unutilized. In cycle 0, the 95 Ah $L^{-1}$ (charge 0) and 49 Ah $L^{-1}$ (discharge 0) capacities account for 51% and 26% of the theoretical charge capacity, respectively, as calculated from the total mass of quinone in the battery. One possible explanation for the low capacity utilization is the phase behavior of
the NQE:PIL (Im) electrolyte. The cell is tested at 90 °C, and both the oxidized form of
the electrolyte and the 50-50 mixture are observed to be liquid at this temperature. Because
the melting point of the reduced species mixture is unknown, it is possible that once the
hydroquinone-rich electrolyte compositions are reached, quinone material is lost to a solid
phase and can no longer be utilized. Small quantities of white precipitate have been observed
upon cell disassembly, which supports this interpretation (SI Fig. S32).

To understand this further we test a quinone-rich, capacity limited (CL) naphthoquinone
eutectic electrolyte composition, which we refer to as NQE:PIL-CL. Like the NQE:PIL (Im)
electrolyte, this mixture contains a 5:1 molar ratio of quinones:Im-ImTFSI, but here the
naphthoquinone is a 10:1 ratio of quinone:hydroquinone. In this configuration only 18 mol%
of the quinone electrolyte’s theoretical capacity can be reversibly charged and discharged in
the symmetric cell, due to the limited quantity of reduced species. The rest of the electrolyte
remains in the oxidized form, resulting in a cyclable RAE concentration of 1.3 M. Cycled at a
rate of 1 mA cm$^{-2}$ at 85 °C, the capacity limited symmetric cell reached 40% of theoretical
capacity on discharge 0, (Fig. 7). This is a larger fraction of the theoretical capacity than
the cell with the fully-concentrated NQE:PIL electrolyte (26%), despite the much faster
charging rate in the NQE:PIL-CL cell. Further diluting the NQE:PIL-CL electrolyte with
ACN, we see increased capacity utilization as the ratio of inert solvent increased, with a
maximum of 72% capacity utilization for a cell diluted with ACN in a 1:1 volume ratio (Fig.
7). Additionally, the realization of over 50% of the theoretical capacity, as calculated for a
2-electron process, further suggests that we are indeed accessing 2-electron quinone redox
under these conditions.

We probe the impact of electrolyte viscosity by diluting the NQE:PIL-CL with the inert
NSPIL rather than ACN. We do not see an improvement in performance (Fig. 7, SI Fig.
S31), and only 21% capacity is utilized at 85 °C and 1 mA cm$^{-2}$ for the NQE:PIL-CL
electrolyte diluted with Im-ImTFSI NSPIL in a 1:1 molar ratio. Because the active species
concentration and charging rate are directly comparable to the 1:1 (NQE:PIL-CL):ACN
experiment, but the capacity utilization is not, this indicates that high electrolyte viscosity also contributes to poor capacity utilization. Though tested in a static configuration in this work, testing these electrolytes in a flow cell configuration with improved mass transport may be one way to achieve improved performance.

Another possible reason for low capacity utilization is kinetic limitations. The large peak splitting observed during cyclic voltammetry of dilute quinone in ACN also suggests slow kinetics for these redox couples with the NSPIL electrolyte (Fig. 5). Using the NQE:PIL-CL electrolyte, we assess this using potentiostatic cycling at 300 mV, holding the voltage until the current reached a lower limit. In this experiment 46% of theoretical capacity is reached on the first discharge, a slight improvement compared to the 40% of capacity reached in the galvanostatic cycling experiment at 1 mA cm$^{-2}$ (SI Fig. S29). We also see improvements in capacity utilization when cycling at a lower rate, suggesting that kinetic limitations also contribute to the limited capacity utilization.

Finally, poor capacity utilization at high redox-active species concentration has also been reported in other highly concentrated organic electrolytes. Quinones and viologens have both been reported to undergo concentration-dependent degradation processes, including dimerization, which have been found to decrease the accessible redox capacity. The elevated temperatures used here may also accelerate any chemical degradation processes, resulting in capacity decay.

**Conclusions and Outlook**

We have proposed and demonstrated an entropically-driven eutectic mixing approach to engineer highly energy-dense electrolytes without added solvent. These electrolytes can achieve both high redox-active concentrations and low viscosity, and can remain liquid in all states of charge due to eutectic melting point depression. Using quinones (and hydroquinones) as a model system, we show that excellent properties can be achieved using low-molecular weight
Figure 7: Capacity utilization during galvanostatic cycling for quinone rich, capacity-limited naphthoquinone eutectic static cells with Im-ImTFSI supporting electrolyte. Discharge capacity, reported as a fraction of theoretical capacity, is compared for NQE:PIL-CL symmetric cells containing a 10:1 ratio of oxidized:reduced quinone species. Cells are cycled at 1 mA cm$^{-2}$ for electrolytes at 3 levels of dilution in ACN. 1:0 (NQE:PIL-CL): ACN (85°C), 1:0.33 (NQE:PIL-CL):ACN (60°C), and 1:1 (NQE:PIL-CL):ACN (60°C), and dilution with Im-ImTFSI NSPIL in a 1:1 (NQE:PIL-CL):NSPIL ratio (85°C).
benzoquinones (16.8 M RAE, 1.95 mPa·s for BQE), and we demonstrate how melting point, ionic conductivity, and viscosity change across various states of charge. We also identify trends corresponding to molecular weight of active species which can guide the design of new eutectic electrolytes, with smaller molecules resulting in mixtures with lower melting points, higher concentrations, and lower viscosities. With the more chemically-stable naphthoquinone eutectic and a NSPIL supporting electrolyte, NQE:PIL (Im) with 7.1 M RAE, we show reversible cycling that reaches a volumetric capacity of 49 Ah L\(^{-1}\) on the first discharge. Here, we have demonstrated proof-of-concept for a eutectic quinone flow battery electrolyte, and substantial optimization and engineering will be needed to understand the performance limits. Building on this foundation, the entropy-driven eutectic mixing approach can be applied to other systems of quinones, or further generalized to other redox-active organic motifs. By using higher-component mixtures, lower-melting mixtures can be achieved, potentially resulting in electrolytes which can operate at room-temperature. Additionally, the use of molecules with intrinsic ionic conductivity in both the oxidized and reduced state could eliminate challenges associated with supporting electrolytes, including reactivity and slow redox kinetics, and the resulting decrease in RAE concentration. Overall, the approach and results presented here enable continued discovery and development of energy-dense and solvent-free eutectic electrolytes for flow batteries.

**Experimental Section**

**Materials**

Chemicals were purchased from commercial suppliers Sigma-Aldrich, Alfa-Aesar, and Ambreed. 2,3-diethyl-1,4-napthoquinone (DENQ) and 2,3-diisopropyl-1,4-napthoquinone (DIPNQ) were purchased from ACME Bioscience (Palo Alto, CA). All chemicals were used as received excluding those synthetically modified as described below.
Hydronaphthoquinone Synthesis

Hydroquinone analogues of DENQ and DIPNQ (referred to as DENQ-H and DIPNQ-H, respectively) were synthesized from their oxidized naphthoquinone counterparts via a chemical reduction with tin (II) chloride.\textsuperscript{64} 1 gram of oxidized quinone precursor was dissolved in 10 mL of synthesis-grade ethanol, warmed at 60 °C. Separately, 4 g of tin (II) chloride (white crystalline flakes) was added to 4 mL of concentrated (12 M) hydrochloric acid (HCl) and stirred until fully dissolved. The SnCl\textsubscript{2} - HCl mixture was then immediately added to the naphthoquinone - ethanol mixture via pipette. The solution immediately turned dark brown, then subsequently stratified into three layers. The top layer was yellow (residual quinone), the middle layer was dark brown, and the bottom layer was clear with white crystals (SI Figure S22). Within 30-60 minutes the hydronaphthoquinone precipitated out of the bottom layer as white crystals with a pink tint. The top two layers of the mixture were removed with a pipette, then the bottom layer was vacuum filtered to collect the hydronaphthoquinone product (washed with deionized water). The oxygen-sensitive product was then stored in an argon glovebox.

The same procedure was applied to both DENQ and DIPNQ to synthesize the hydroquinones DENQ-H and DIPNQ-H, respectively. Yield of the DENQ-H product was ~80%. For DIPNQ-H, NMR indicated that the product was a mixture of the hydroquinone and precursor quinone with ~50% conversion. NMR spectra of hydronaphthoquinone synthesis products are shown in SI Figures S23 and S24.

Protic Ionic Liquid Synthesis

Non-stoichiometric protic ionic liquids (NSPILs) were prepared at 50 percent protonation in an argon glovebox. Organic bases (pyridine, 1,2,4-triazole, imidazole, triethylamine) were mixed with bis(trifluoromethylsulfonyl)imide in a 2:1 molar ratio. The mixtures were heated until liquid, then stirred for 1 hour on a hotplate. NSPILs were stored in an argon glovebox.
Eutectic Mixture Preparation

To prepare eutectic quinone mixtures, individual components were massed and mechanically mixed for at least 1 minute, either using a mortar and pestle or by stirring with a spatula, to form a homogeneous mixture. NQE:PIL (Im) samples for symmetric cell cycling and ionic conductivity measurements were mixed in a glovebox under argon, and all other samples were prepared in air.

Thermal Characterization

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC Q2000. The instrument was periodically calibrated with an empty cell to acquire a baseline, a sapphire standard to calibrate heat capacity, and with an indium standard to calibrate melting temperature and enthalpy of melting. Components of multi-component mixtures were mixed in equimolar ratios unless otherwise specified. DSC experiments were typically carried out using a heat - cool - heat protocol. The initial heat step used a 10 °C/min ramp rate to pre-melt and homogenize the sample. The samples were then cooled back down to room temperature (cooling ramp rates were adjusted depending on the rate of sample recrystallization). The samples were heated again in the second heat step at 1 °C/min. The melting temperature was determined from the peak onset point of the second, slower heating step, defined as the intersection point of the slope tangent with the baseline.

Viscosity Measurement

Viscosity was measured using an ARES-G2 Rheometer using a cone-plate geometry with a 40 mm, 2 degree cone. The zero gap was calibrated before measurement at each temperature. Approximately 0.6 g of sample was used for each measurement. Data was collected using a “flow sweep” protocol between shear rates of 1-1000 s⁻¹. All liquids appeared Newtonian throughout the range of shear rates tested, and the viscosity at a shear rate of 400 s⁻¹ is
Ionic Conductivity Measurement

Ionic conductivity was measured using a Biologic MCS10 ionic conductivity spectrometer with temperature control. Roughly 700 µL of sample was prepared and transferred to an ionic conductivity tube. The temperature profile consisted of 5 °C steps with a 5 minute hold at each step and 2 hour holds at 60 °C and 85 °C.

Cyclic Voltammetry

All electrochemical experiments were performed using a Biologic SP-300 potentiostat. Cyclic voltammetry was conducted under argon in a 3-electrode cell with a glassy carbon working electrode (2.5 mm radius, Pine), Pt wire counter electrode (0.5mm dia, 99.9%, Sigma), and Ag wire quasi reference electrode (0.5mm dia, 99.99%, Sigma). Prior to each measurement, the glassy carbon electrode was polished using 0.05 µm alumina and the Ag wire was cleaned in nitric acid solution. Potentials were referenced to the ferrocene-ferrocinium redox couple (Fc/Fc⁺). Due to overlap between the redox peaks of the samples and the reference compound, the internal standard was was added after the initial measurement.

Symmetric Cell Testing

A low volume static cell was custom built for cycling experiments. 6-16 µL of electrolyte was pipetted onto carbon cloth (0.5 cm², ELAT-H plain cloth, Fuel Cell Store) electrodes in contact with glassy carbon current collectors (SPI Supplies), sealed by rubber gaskets to contain the electrolyte. Two symmetric sides were separated by a modified Nafion 212 membrane (Fuel Cell Store) which was saturated in imidazole-imidazolium bis(trifluoromethylsulfonyl)imide NSPIL (75 °C, 1 hour) prior to cell assembly. All cell components were prepared, assembled, and cycled in an argon glovebox. Measurements at elevated temperatures were conducted.
on a hotplate.

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