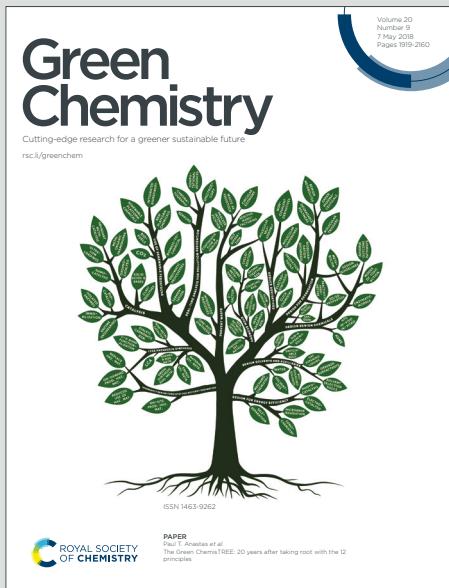


Green Chemistry

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1. This work introduces glycerol as a safer, low-cost alternative to the toxic and thermally unstable carbonate solvents used in sodium-ion batteries, opening wide opportunities for high-voltage batteries based on sustainability, safety, and resource circularity.
2. Unlike other safe electrolytes, e.g. aqueous, we demonstrate that highly concentrated NaFSA–glycerol electrolytes can achieve wide electrochemical stability windows up to ~4.3 V which enables stable contact with Na metal. Furthermore, the glycerol electrolytes, which are biodegradable and a byproduct from industrial processes, also suppress dissolution of organic electrode materials during charge/discharge cycling.
3. These are the first electrolytes to be prepared from glycerol for battery applications, but future work will focus on replacing NaFSA with other more environmentally friendly electrolyte salts. Further optimization, focusing on dilute electrolytes and exploring green co-solvent systems may improve ionic conductivity while maintaining safety and sustainability.



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Glycerol Electrolytes for Safer and More Sustainable Sodium Ion BatteriesReceived 00th January 20xx,
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To move toward greener, less toxic and less flammable solvents for sodium-ion batteries (SIBs), we demonstrate the first glycerol-based electrolytes for battery applications. Mixtures were prepared using glycerol with $\text{Na}[\text{N}(\text{SO}_2\text{F})_2]$ (NaFSA) up to a molar ratio of 1:0.8 (NaFSA:glycerol) maintaining a neat liquid state, nonflammability, and good electrochemical stability compared with other green solvents like water. Furthermore, even higher electrochemical stability was observed for mixtures containing urea, e.g. NaFSA:glycerol:urea of 1:0.5:0.5, up to 4.3 V. Despite the protic nature of glycerol, we observe reasonable stability in contact with Na metal and indications of reversible plating/stripping for potential applications toward high-voltage batteries. Next, we target the combination of relatively dilute 1:5 NaFSA:glycerol electrolytes with metal-free organic electrodes for reducing the excess electrolyte recently applied in aqueous batteries. Due to the high innate viscosity of glycerol, we find that even at relatively low electrolyte concentrations major improvements in cyclability and dissolution are observed compared with similar concentration aqueous electrolytes. We further show stable charge/discharge cycling over 250 cycles. Overall, these electrolytes show interesting opportunities for optimization to maximize performance while moving toward safer and greener next-generation batteries.

Currently, the most widely used electrolytes in alkali ion batteries are based on mixed carbonates (e.g. ethylene carbonate) as well as a growing interest in linear ethers, or glymes.^{1, 2} However, despite the observed high performance, these electrolytes tend to be flammable, toxic, or explosive depending on the solvent mixture.^{3, 4} This has driven interest in developing safer battery electrolytes for future technologies. At the same time, we also have targets of low-cost and renewable

materials for the electrodes and battery materials as a major selling point of transitioning toward sodium ion batteries (SIBs) compared with lithium ion batteries (LIBs).^{5, 6} It is intuitive to also target low-cost, safe and renewable components for the liquid electrolyte. However, a major hurdle for moving to new and safer electrolytes, is the impact of electrolyte composition on interphase chemistry at the positive and negative electrodes leading to a daunting task for electrolyte development.

It is well known that the electrolyte plays an essential role in enabling fast transport of Na^+ between the cathode and anode during charge and discharge, but it also must decompose to form stabilizing interphases, such as the solid electrolyte interphase (SEI) to attain high voltages.⁷⁻⁹ The electrochemical stability of water, a top choice as a green solvent for batteries,^{10, 11} remains significantly poor compared with organic electrolytes.¹² Even with the development of highly concentrated aqueous electrolytes (i.e. water-in-salt electrolytes (WISE),¹³⁻¹⁵ high capacity materials like carbon (e.g. hard carbon, graphite) and alkali metal plating/stripping for aqueous alkali ion/metal batteries cannot be utilized.¹⁶ The requirement of high electrolyte concentrations are also a costly drawback that limits commercial practicality. Furthermore, the aqueous conditions can easily solubilize or react with some active materials.^{17, 18} Aside from water, our group has also been exploring non-flammable deep eutectic electrolytes (DEEs) using urea derivatives and lithium bis(fluorosulfonyl)amide (LiFSA) for LIBs.¹⁹ Though urea is also a low cost, sustainable and non-flammable material, its mixtures with sodium bis(fluorosulfonyl)amide (NaFSA) do not tend to form DEEs that are liquid at room temperature (Fig. S1). Thus, other green solvents should be considered for attaining higher stability electrolytes for next-generation SIBs.

Herein, we target glycerol as one of the most promising and cost-effective (Table S1) green solvents for batteries due to its biodegradability, safety, and abundance as a waste product from multiple chemical industries and derivability from biological sources.²⁰⁻²² Glycerol is a trihydric alcohol and protic

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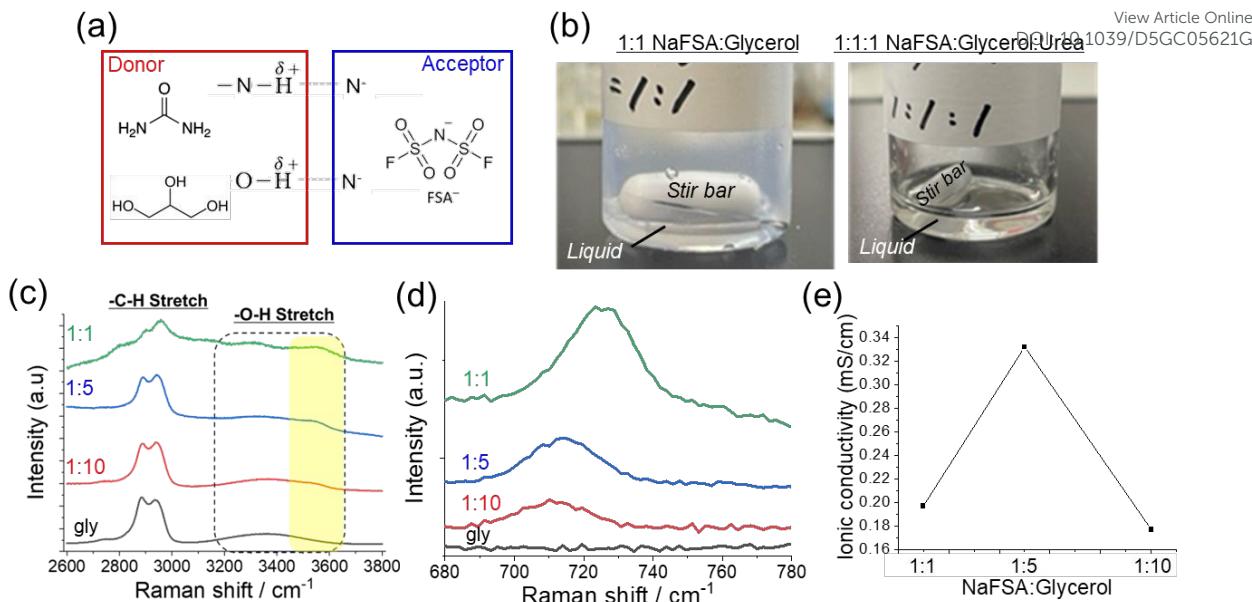


Figure 1. Preparation and electrolyte characterization. (a) Donor-acceptor behavior in DEE and glycerol electrolytes. (b) Highly concentrated electrolytes prepared with NaFSA and glycerol or urea-glycerol mixtures. Raman spectrum for regions associated with (c) O-H and (d) S-N-S. (e) Ionic conductivity of select glycerol electrolytes.

solvent and shows interesting thermal properties, compatibility with a wide variety of electrolyte salts,²³ and unlike other alcohols, is considered relatively non-flammable. Only a few studies have explored the incorporation of glycerol into aqueous and other electrolytes for battery applications,^{24, 25} where it improves the electrochemical stability. However, no battery electrolytes have been prepared using glycerol as the sole solvent to the best of our knowledge. Only one recent work shows the development of an eco-friendly NaCl-glycerol electrolyte for usage with double layer capacitors.²⁶ Interestingly, glycerol shows similar properties to urea and DEEs by utilizing donor-acceptor interactions (Fig. 1a). We found that glycerol can attain neat mixtures with NaFSA at various mol/mol (= NaFSA:glycerol) ratios $\geq 1:1$ as shown in Fig. 1b and Fig. S2. This solubility is quite high among other organic electrolytes and aqueous solutions (Table S2). Furthermore, glycerol can directly incorporate other green solvent species like urea,²⁵ to attain very high NaFSA concentrations (1:0.5:0.5, NaFSA:glycerol:urea, or >4 mol dm⁻³). In all, glycerol appears to be a highly versatile base solvent for preparing battery electrolytes.

To understand the intermolecular interactions between Na⁺, bis(fluorosulfonyl)amide anion (FSA⁻), and glycerol, we evaluated the solvation structure using Raman spectroscopy. For the NaFSA:glycerol electrolytes, we observed a secondary peak in the O-H region (3200–3700 cm⁻¹) which is not observed in pure glycerol (Fig. 1c). This other peak is indicative of the breaking of the hydrogen bonding network within the glycerol solution when the NaFSA is introduced. As the concentration increased further, this peak became more prominent. We also observed the appearance of the peaks for S-N-S (700–750 cm⁻¹) (Fig. 1d) and S=O (1200–1220 cm⁻¹) stretching modes of FSA⁻ (Fig. S3). As the concentration of NaFSA increased, a shift in the peak positions to higher wavenumbers occurred like previous reports with concentrated LiFSA electrolytes.^{27, 28} This indicates

the formation of complex ion structures, or aggregates, between the FSA⁻ and alkali ions.^{19, 29} We note some difficulty resolving the S-N-S region for the 1:1 electrolyte with a green laser (532 nm) due to overwhelming fluorescence (Fig. S4). As shown in Fig. 1d, we could resolve the S-N-S peak shift by alternatively employing a red laser (785 nm). This result clearly indicates ion clustering with increasing concentration of the electrolyte.

The ionic conductivities were further evaluated at 25 °C for a few different NaFSA concentrations (Fig. 1e), i.e. 1:10, 1:5 and 1:1, for low middle, and high NaFSA concentrations, respectively. We found the highest ionic conductivity for the 1:5 electrolyte showing 0.332 mS cm⁻¹, which is similar to some reported DEEs.¹⁹ The 1:1 and 1:10 electrolytes showed a bit lower ionic conductivities of ~ 0.197 and 0.177 mS cm⁻¹, respectively. Such inversions in conductivity are well known to occur in carbonate electrolytes. Aside, the conductivity of the 1:0.5:0.5 NaFSA:glycerol:urea electrolyte was even lower at 0.084 mS cm⁻¹ due to its very high viscosity.

It is known that glycerol has some unique and interesting thermal properties, including a high freezing point of 18 °C, but is often observed as a liquid phase due to supercooling.³⁰ To investigate the thermal behavior of the glycerol electrolytes, we used differential scanning calorimetry (DSC). We increased the sample temperature from room temperature to 120 °C, then decreased the temperature to -100 °C at a rate of 10 °C/minute for all samples (Fig. 2a). For pure glycerol, no peaks were observed until a glass transition event with a glass transition temperature (T_g) of ~ -75 °C. As NaFSA was dissolved into glycerol in a ratio from 1:10 (~ 1 mol dm⁻³) up to 1:4 (~ 3.4 mol dm⁻³) we observed minimal changes in the DSC results with only a slight shift toward more positive T_g. At higher NaFSA concentration, T_g continued to shift to higher temperatures, but remained below -25 °C up to a ratio of 1:1. Similar low T_g have

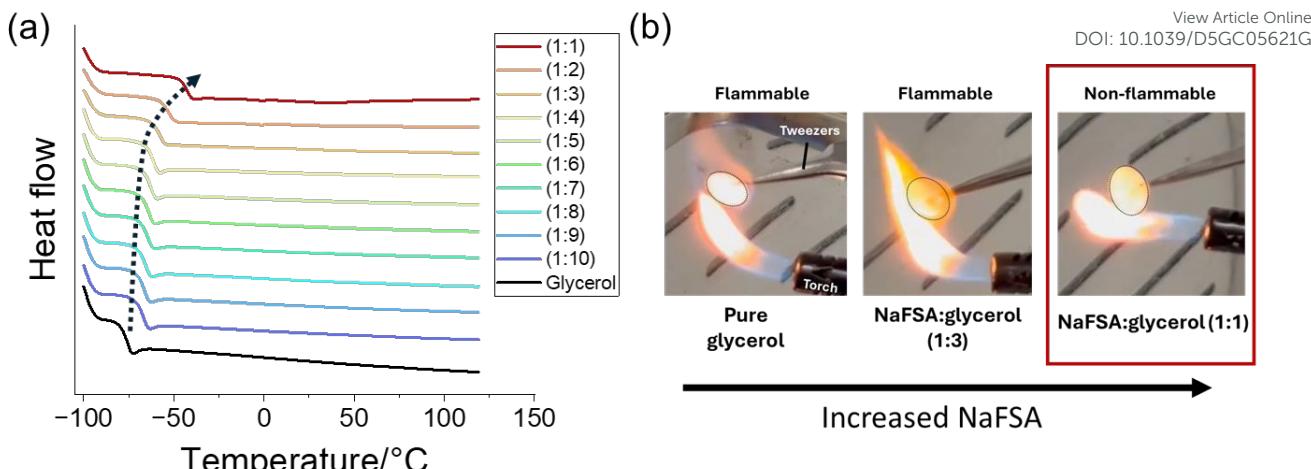


Figure 2. Thermal properties. (a) DSC freezing curves of NaFSA/glycerol electrolytes. (b) Photos of flammability test of glycerol electrolytes. Original videos are provided as supplemental files.

been observed for other electrolytes prepared with glycerol.³¹ At 1:1, we could also observe a small and broad peak which may further indicate solidification or phase separation (Fig. S5) though the electrolyte appeared as a liquid. Nevertheless, glycerol maintains a liquid state across a wide range of electrolytes concentrations and temperatures. Likewise, the DSC of the glycerol/urea electrolyte (1:0.5:0.5) showed a similar low temperature T_g (Fig. S6).

In addition to low temperature stability, we also evaluated the high temperature stability of our electrolytes. Using thermogravimetric analysis, the glycerol electrolytes were found to be significantly more stable than commercial carbonate-based electrolytes (Fig. S7). The flammability was also evaluated in direct contact with an open flame. Pure glycerol has a significantly higher flashpoint (> 150 °C) than many carbonate electrolytes but still ignites upon exposure to a flame (Fig. 2b, Supplemental Video 1). When the fluorine-based NaFSA was added to 1:3, we observed reduced flammability though a polymerization type reaction was also initiated (see Supplemental Video 2). A similar reaction was also observed for

the 1:0.5:0.5 NaFSA, glycerol, and urea electrolyte (Supplemental Video 3). This type of reaction is observed during thermal decomposition of sugars and intumescent paints, producing a carbon-based char that can help resist further combustion. With further addition of NaFSA to 1:1, we observed no ignition and non-flammability for ~ 8 s of contact with the flame (Supplemental Video 4). From these results, it is apparent that glycerol does not have any inherent non-flammability, but it has high compatibility with fluoride salts or other additives that can potentially make it non-flammable or resistive toward combustion.

We further characterized the electrochemical properties of the NaFSA/glycerol electrolytes using linear sweep voltammetry (LSV) at Pt and Al foils for the positive and negative scans, respectively. As shown in Fig. 3a, the 1:5 electrolyte showed a good electrochemical stability window of near 3 V; which is similar to WISEs even though the concentration of NaFSA is significantly lower at about 2.7 mol/kg. We did not see a significant change for 1:3, but the oxidation and reduction resistance were notably improved as the mixture reached 1:1.

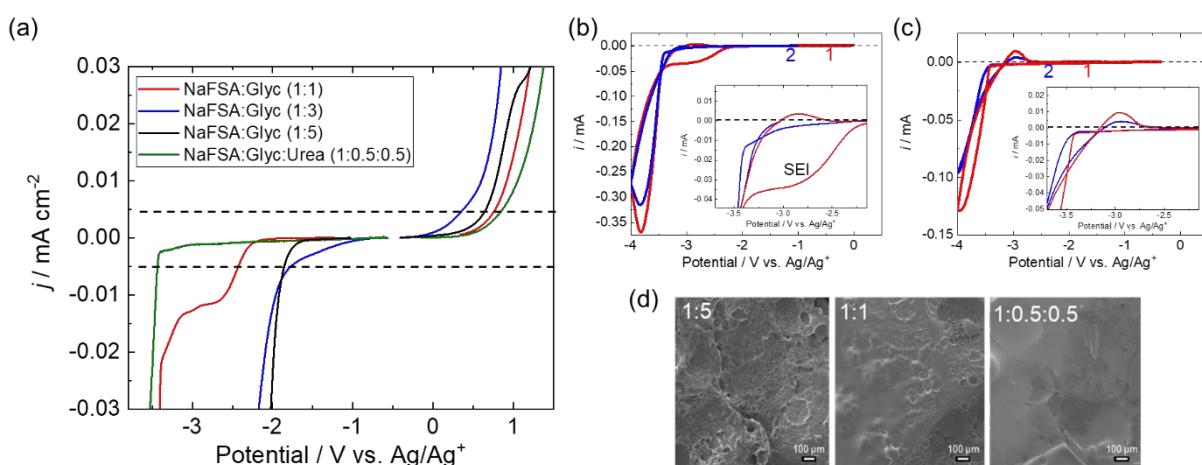


Figure 3. Electrochemical stability. (a) Linear sweep voltammetry of NaFSA electrolytes. Plating/stripping of Na metal in (b) 1:1 NaFSA:glycerol, and (c) 1:0.5:0.5 NaFSA:glycerol:urea electrolytes, conducted at 0.5 mV/s. (d) SEM of Na metal surface after soaking for 4 days in each electrolyte.

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For this electrolyte, the decomposition was observed below -2.4 V vs. Ag/Ag⁺. Since urea and its DEE are also considered green solvents and we recently reported DEE of LiFSA-urea, we also evaluated the 1:0.5:0.5 NaFSA:glycerol:urea electrolyte. We found that, this ternary liquid further extended the potential window to ~4.3 V with cathodic decomposition below Na plating (~-3.0 V vs Ag/Ag⁺). This provides some opportunity for application in alkali metal batteries which require high cathodic stability.

To further test the potential for usage of Na metal as a negative electrode material, we tested for reversible plating and stripping of Na on an Al foil current collector (Fig. 3b,c). Though the reversibility was not high in both cases, it is interesting that two protonic solvents like glycerol and urea can be stabilized at the surface of freshly deposited Na metal. In addition, for the 1:1 electrolyte, we observed an initial cathodic peak at -2 V that disappears in the 2nd cycle. Such events can be evidence of a growing and stabilizing SEI.^{7, 19} For the 1:0.5:0.5 electrolyte, the stripping peak was better defined, but the broad reduction peak suggesting "SEI" growth as well as possible hydrogen evolution were not observed.

Generally, urea and glycerol electrolytes react strongly with alkali metals, but the LSV and stripping results suggest their mixtures can stabilize at the Na surface. We conducted further tests of the stability of these electrolytes in contact with Na metal (Fig. S8). As shown in Fig. 3d using SEM, we observed significant roughening of the Na metal surface after soaking in the 1:5 electrolyte for 4 days, while the Na metal surface remained noticeably smoother for the 1:1 or 1:0.5:0.5 electrolytes. Also, we note significant gas and bubble formation only for the 1:5 electrolyte in agreement with the roughened surface seen under SEM. We note that the surface remains

stable during soaking, but we can anticipate that cycling of Na metal in these electrolytes may lead to further electrolyte decomposition and surface roughening. Nevertheless, the behavior majorly contrasts with aqueous electrolytes which violently react with alkali metals. As with DEEs and other highly concentrated electrolytes, it is possible that the strong bonding between the electrolyte ions and the solvent species lead to such improved stabilization. We speculate the solution structure may inhibit contact and hydrogen evolution at the Na metal surface. We also considered the possibility of SEI formation that protects the Na surface and found that F- and S-species were observed using energy dispersive x-ray spectroscopy (Fig. S9). However, we note that glycerol electrolytes are difficult to remove with commonly used solvents like diethyl or dimethyl carbonates. We cannot fully rule out residual electrolyte and improved washing conditions as well as in situ analyses will be considered for future work. Overall, the stability of Na metal and access to these low potentials appears to be promising where glycerol electrolytes show similar electrochemical stability to other organic electrolytes and opportunities for stable SEI compared with aqueous electrolytes.

Aside from accessing low voltage electrodes, another target for next-generation battery electrolytes is to reduce the high electrolyte concentrations as used in aqueous and DEEs. These high concentrations, above 5 mol/kg, lead to major additional costs and reduce the practical aspects of the developing technologies. For more sustainable green batteries, we focus on the 1:5 NaFSA/glycerol electrolyte which only contains ~2.7 mol/kg salt. We considered the electrode materials 3,4,9,10-perylenetetracarboxylic acid-dianhydride (PTCDA) and 3,4,9,10-perylenetetracarboxylic diimide (PTCDI), which are based on

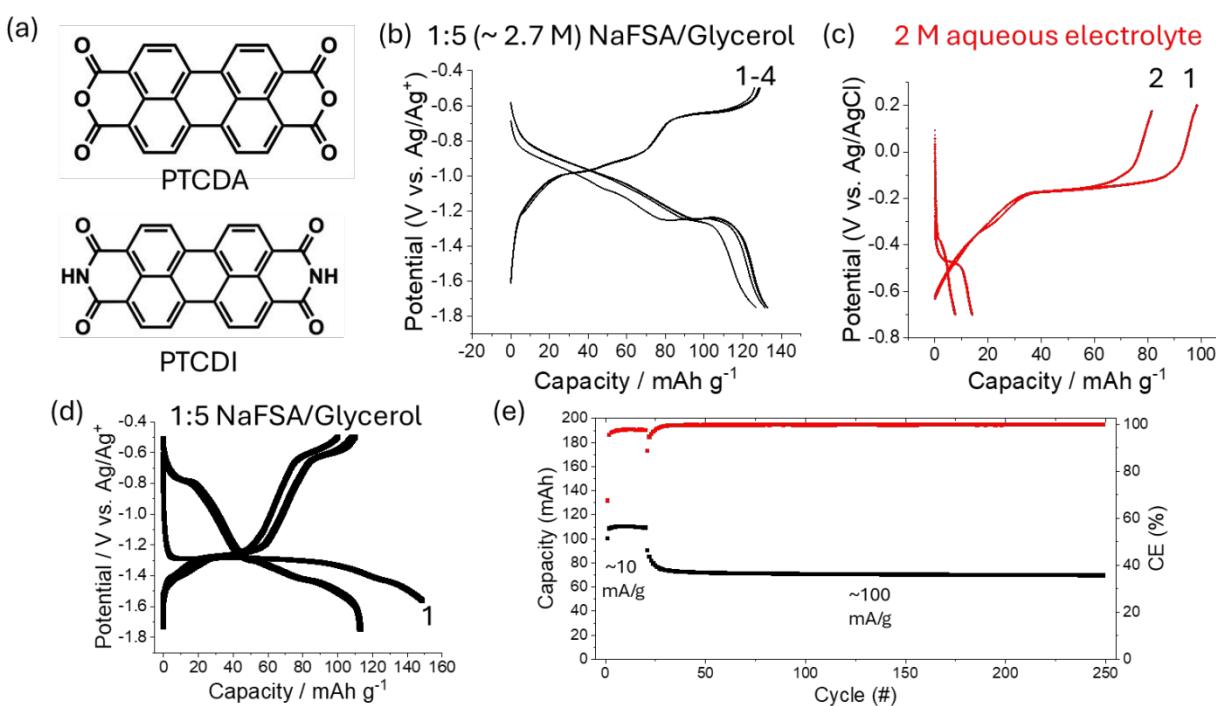


Figure 4. Application in energy storage. (a) Structures of PTCDA and PTCDI. Charge/discharge tests of PTCDA in (b) 1:5 NaFSA/glycerol, and (c) 2 M aqueous electrolytes. (d) Charge/discharge curves and (e) long term cycling of PTCDI in 1:5 NaFSA/glycerol.

Table 1. Green and battery metrics for glycerol electrolyte usage in batteries.

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Solvents	Non-toxic	Compatible with non-toxic salts	Renewable	Biodegradable	Voltage window (V)	Flammability
Aqueous	X	X	X	X	2.8 ¹²⁻¹⁴	Non-flammable
Glycerol	X	X ²²	X	X	3.2-4.3	Low
Carbonate	-	-	-	- ³⁶	4-5 ^{37,38}	High
Glymes	-	-	-	- ³⁶	4-4.5 ³⁸	High

organic compounds free from 3d metals (Fig. 4a). These materials can be naturally abundant, inexpensive, non-toxic and biodegradable, and have been explored for batteries in recent years.³²

We prepared composite electrodes containing PTCDA, conductive carbon, and PVDF binder (7:2:1 by mass) and conducted galvanostatic charge/discharge tests. A key challenge for using PTCDA and many other organic electrodes is dissolution of the active material during cycling in both organic and aqueous electrolytes.^{33, 34} At times, this issue has been partially resolved by using highly concentrated WISEs showing high viscosity.³⁵ Here, we evaluated the impact of the inherent high viscosity of glycerol-based electrolytes on the dissolution of PTCDA. As shown in Fig. 4b, PTCDA can stably cycle (rate of 13.7 mA/g) in our 1:5 NaFSA/glycerol electrolyte with good Coulombic efficiency (CE, >99%) and stable reversible capacities of ~130 mAh/g; very close to the theoretical capacity of 137 mAh/g. Generally, this material shows low reversible capacities near ~70 mAh/g.^{32, 36, 37} If we look at the charge/discharge of PTCDA at a similar rate (16.66 mA/g) and in a similar concentration aqueous electrolyte (based on 2 M NaCl), the material does not successfully cycle. Instead, we cannot access the lower potential plateau and observe rapid dissolution and cross-over during the charge-discharge process. This was also apparent from changes in color of the electrolyte after reducing the PTCDA electrode in the aqueous electrolyte (Fig. S10). If PTCDA is reduced in the 1:5 glycerol electrolyte and stored for >12 hours, we observe no dissolution into the electrolyte with a stable and reduced OCP (Fig. S11). On the other hand, if the electrode is moved to a 2 M NaCl electrolyte (aqueous); a color change occurs immediately and becomes more intense over a couple hours. Likewise, higher concentrated electrolytes like 1:1 also show stable cycling behavior with PTCDA (Fig. S12). Overall, glycerol electrolytes are quite effective for improving issues with dissolution for organic electrodes. We suspect this may be linked to the electrolytes' solution structures that lead to differences in the interaction with the small organic molecules within the composite electrode, i.e. differences in solubility of the active material, but there also may be some role of SEI or interphase structures on the improved stability.

Next, we further tested the long term cyclability of another organic electrode, PTCDI, which has a similar structure to PTCDA but is more resistant to dissolution. As shown in Fig. 4d,e, we started cycling the cell at a charge/discharge rate of 10.3 mA/g

(~0.075 C based on a theoretical capacity of 137 mAh/g) and obtained ~ 109 mAh/g and a CE of 97.5% after 20 cycles. The slightly low CE is potentially due to gradual electrolyte decomposition during slow charge/discharge. If PTCDI was polarized to lower potentials (~2.2 vs. Ag/Ag⁺), we tended to observe electrolyte decomposition (Fig. S13) which contrasts somewhat with our LSV results in Fig. 3. We suspect this is related to higher reactivity of the conductive carbon additive with the electrolyte. Not only SEI formation and stability but also electrocatalytic property and specific surface area of the conductive carbon may play a role. Thereafter, the rate was increased to 103 mA/g for more extended cycling. In this case, the average CE was high (99.71%) and the capacity retention was 97.1% after stabilization (from cycle 50-250). Further cycling studies of these electrolytes are ongoing in our laboratory, including the pursuit of positive electrodes for demonstration of a full cell.

To conclude the analysis, we compare our glycerol electrolytes with other electrolyte systems to highlight their green advancement (Table 1). For our comparison, we focus on the battery solvent, because much of the chemistry and benefits are altered by changing the electrolyte salt. We find that like aqueous electrolytes; glycerol is unique in that it is non-toxic and compatible with non-toxic electrolyte salts. Most battery electrolytes (including current high performance aqueous electrolytes) rely on salts such as NaFSA or NaPF₆ to attain their high performance. Hopefully these salts can be replaced in future batteries, but many safe alternative salts, such as sodium acetate, are poorly soluble in commonly used battery solvents. In other words, electrolytes based on carbonates and glymes *will generally consist of mixtures of toxic solvents with toxic salts*. Glycerol also aligns well with aqueous systems in terms of renewable origin and ease of biodegradability compared with carbonates and glymes.³⁸ Coming to the metrics related to batteries, we see that glycerol is approaching high voltages like other organic electrolytes^{39, 40} while maintaining low flammability due to its low vapor pressure. Even in this first iteration, the voltage capabilities of glycerol electrolytes are significantly improved over aqueous systems. Considering overall electrolyte cost, it is noteworthy that the most electrochemically stable glycerol electrolytes, like highly concentrated aqueous electrolytes, rely on a significant amount of electrolyte salt which will increase the cost. Thus, looking to replacing costly and toxic electrolyte salts as well as

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moving toward leaner glycerol electrolytes will be an important step for future work and next-generation batteries.

Conclusions

In this work, we explored a unique, versatile and low-cost solvent system, glycerol, for preparation of electrolytes for SIBs. Glycerol can be mixed with fluorosulfonamide salts (e.g. NaFSA) up to a molar ratio of 1:0.8 (NaFSA:glycerol) as well as form highly concentrated electrolytes with a urea co-solvent. Much like DEE, Raman indicates the solvation structure includes ion clustering and disruption of the hydrogen bonding network within glycerol. The addition of high concentrations of NaFSA are shown to improve temperature stability and even impart nonflammability. Furthermore, we find high electrochemical stability with measured potential stability windows of ~ 3.2 V and ~ 4.3 V for 1:1 NaFSA/glycerol electrolytes and 1:0.5:0.5 NaFSA:glycerol:urea electrolytes, respectively. The improved reduction stability compared with water even allows contact with Na metal without continuous reaction. Unfortunately, when evaluating Na plating/stripping and composite electrodes, we find issues with maintaining a stable SEI for continuous cycling of low redox potential battery materials and further work is needed in the future. Thereafter, we considered relatively dilute glycerol electrolytes as an alternative to WISEs. Charge/discharge testing using organic electrode materials showed that even under these concentrations, the innate viscosity of glycerol can significantly improve electrode dissolution leading to stable cycling over 250 cycles with high CE. In all these electrolytes are in early development, but they show interesting properties and opportunities for improving the safety of next-generation batteries from multiple angles.

Author contributions

Z.T.G.: Conceptualization, Investigation, Formal Analysis, Writing – original draft, and Supervision. T.F.: Investigation, Formal analysis. T.H.: Formal analysis, Writing – review & editing. K.S.: Investigation, Formal analysis. S.K.: Supervision, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data are provided in the manuscript or in the Supplementary Information file. Supplementary Information: experimental details, additional photographs of the electrolyte, additional Raman and DSC results, thermogravimetric analysis, photographs of Na metal stored in glycerol electrolytes and EDX analysis of the Na metal surface after soaking, PTCDA dissolution experiments, additional cycling data of PTCDA, electrolyte decomposition at composite battery electrodes. See DOI: X for further details.

Acknowledgments

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All data are provided in the manuscript or in the Supplementary Information file. Supplementary Information: experimental details, additional photographs of the electrolyte, additional Raman and DSC results, thermogravimetric analysis, photographs of Na metal stored in glycerol electrolytes and EDX analysis of the Na metal surface after soaking, PTCDA dissolution experiments, additional cycling data of PTCDA, electrolyte decomposition at composite battery electrodes. See DOI: X for further details.

