An Aqueous Eutectic Electrolyte for Low-Cost, Safe Energy Storage with an Operational Temperature Range of 150 °C, from −70 to 80 °C

Wesley Viola and Trisha L. Andrew*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The performance of conventional energy storage devices greatly suffers at low temperatures. Here, we show that aqueous electrolytes represent an unexpectedly promising solution to this low-temperature issue. The high solubility of lithium chloride in water greatly lowers the freezing point at the eutectic concentration, allowing for a liquid aqueous electrolyte to exist at −74 °C. This electrolyte is used to support low-temperature energy storage in supercapacitors containing an industry-standard activated carbon, retaining 72% of room temperature capacity (28 F/g) at −70 °C and 42% at −80 °C. Since the electrolyte is nonflammable, a high-temperature operation is also possible up to 80 °C, amounting to a broad 150 °C temperature range which covers the most extreme conditions on earth. At −70 °C, the electrolyte has a remarkably high conductivity (1.83 mS/cm) and a broad three-volt stability window. By blending in poly(vinyl alcohol), a polymer electrolyte is made which retains much of the low-temperature performance and is used to make a device capable of lighting an LED at −70 °C for more than a minute. The devices made here excel at low-temperature energy storage and use only safe, low-cost commodity materials.

Eutectic aq. LiCl at −70°C
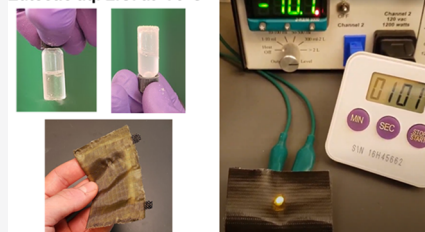
INTRODUCTION

Sustainable, safe energy storage will be key to fully utilizing renewable power sources and enabling new classes of technology. One significant limitation of electrochemical energy storage is performance loss or failure at low (<−20 °C) temperatures. This shortcoming impacts the efficiency of mature technologies such as electric vehicles in cold climates.[1] In more extreme environments, such as polar regions, aerospace, and other potentially habitable planets, the development of certain novel technologies which demand power delivery at −70 °C and colder are even more severely limited. Clearly, a means of low-temperature energy storage is needed.

The lower limit of commercial energy storage devices ranges from about −20 to −40 °C, with supercapacitors being generally more tolerant than lithium-ion batteries.[2] Below these limits, issues arise in the ion-conducting electrolyte where increased viscosity and freezing hamper the mobility of charges. This manifests as an increased ionic resistance which either hurts the efficiency of the device or completely arrests device operation. For most electrochemical devices, the electrolyte is comprised of organic solvents and salts; therefore, much of the work on low-temperature energy storage has focused on these materials.[3−5] Propylene carbonate and acetonitrile are some commonly used examples, with low freezing points around −50 °C. A common approach to extend the temperature range of the electrolyte is to add the low-freezing solvent dioxolane. However, this is a poor electrolyte

solvent (having a high viscosity and low dielectric); therefore, custom electrode materials must be engineered to pair with it.[4] Other efforts include developing low-freezing ionic liquid mixtures matched to activated carbons with, again, specially engineered pore distributions to accommodate bulky ions.[6,7] Such ionic liquids enable energy storage down to −70 °C, but these exotic chemicals have a correspondingly high cost.

Aqueous electrolytes are perhaps an unlikely candidate for low-temperature energy storage. Despite the growing interest in safe and low-cost alternatives to organic electrolytes,[8−10] these materials are little considered in the context of low-temperature energy storage, likely due to the high freezing point of pure water. Here, we demonstrate that a mixture of the commodity salt lithium chloride (LiCl) and water forms an excellent low-temperature electrolyte, supporting energy storage in supercapacitors as low as −80 °C. The electrolyte used is a eutectic mixture of LiCl (24.8 wt %) in water with a greatly depressed freezing point of −74 °C, allowing for remarkably high conductivity (1.83 mS/cm) even at −70 °C. Efficient charging of an off-the-shelf activated carbon (Kuraray) at low temperatures demonstrates the practical

A

nature of the aqueous electrolyte which outperforms a conventional organic electrolyte below −40 °C. Not only does this aqueous electrolyte support exceptional low-temperature charging kinetics, but its stability window also widens from about two to three volts when cooled from room temperature to −70 °C. This aqueous electrolyte is a low-cost, competitive alternative to organic electrolytes for energy storage in extreme environments.

■ MATERIALS AND METHODS

Device Fabrication. Electrodes were made by dip coating carbon cloth (Fuel Cell Earth) in an activated carbon (Kuraray YP-80FP) slurry. The slurry was composed of 90 wt % activated carbon powder, 5 wt % carbon black, and 5 wt % poly(tetrafluoroethylene) (PTFE 60 wt % dispersion, Sigma-Aldrich). A 50/50 mixture of reverse osmosis (RO) water and ethanol were added, and the mixture was sonicated until a thin slurry was formed. Carbon cloth was dip-coated in the slurry and dried in an oven overnight at 100 °C. Carbon cloth was weighed before and after to determine a carbon loading of ∼2 mg/cm^2. Electrolytes used were a 24.8 wt % (7.86 mol/kg) solution of lithium chloride (LiCl; Sigma-Aldrich, >99% purity) in RO water and 0.5 m tetraethylammonium tetrafluoroborate (TEABF$_4$) in acetonitrile. Electrodes were soaked in electrolytes overnight. A gel electrolyte was made by mixing 1 g polyvinyl alcohol (PVA) (Sigma-Aldrich Mowiol 40−88) with 10 mL RO water, heating the mixture to 90 °C, adding 2.125 g of LiCl, and stirring the resulting mixture at 90 °C for 2 h before cooling. Once cooled, the electrolyte was drop cast onto the device (same structure as above), layer by layer. This device was then allowed to dry overnight, open to air in a fume hood. Moisture loss after the drying step was recorded. Supercapacitors were made by sandwiching a cotton separator between two electrodes and saturating with electrolyte. Platinum foil contacts were used to eliminate corrosion of leads. Devices were 0.75 cm^2. A larger (∼8 cm^2) packaged device was made to demonstrate low-temperature power capabilities.

Electrochemical Measurements. Low-temperature measurements were taken in a custom-made chamber (Figure S1). A PID controller (J-KEM Gemini), taking two thermocouple inputs from inside the testing chamber, operated an aquarium pump that bubbled recycled air through liquid nitrogen and into the chamber. A heating element was also used to achieve high temperatures. More details on the chamber are provided in the Supporting Information. Temperature was held within 1.5 °C of the target during testing. Before a measurement was taken, samples were held at the target temperature for at least 10 min.

Cyclic voltammetry of the devices was taken across various temperatures at a scan rate of 5 mV/s using a WaveNow potentiostat (Pine Instruments). Specific capacitance was calculated as $C_{sp} = 4 \times C/m$, where C is the measured capacitance of the two-electrode cell and m is the total mass of the two electrodes. For the devices containing the eutectic LiCl electrolyte, the 12-h temperature hold experiment involved cooling the device to −70 °C, taking a CV measurement, holding at −70 °C for 12 h, and taking another measurement at −70 °C. Charge−discharge cycle stability measurements of these devices were taken at −70 °C and 80 °C using a current of 1 A/g and 2.5 A/g, respectively. Gravimetric energy density was calculated as $E = 0.5 \times C \times V^2$, where C is the gravimetric capacitance and V is the voltage window.

Electrochemical stability measurements for the eutectic LiCl liquid electrolyte were made using a three-electrode cell with a platinum counter and working metal electrode and a Ag/AgCl reference (Chinstruments). The scan rate was 10 mV/s and the threshold for electrolyte stability was taken to be 0.6 mA/cm^2.[9]

Temperature-dependent conductivity of the eutectic LiCl liquid electrolyte was determined by measuring the IR drop in galvanostatic charge−discharge tests (WaveNow potentiostat) of two activated carbon electrodes (area = 0.5 × 1.5cm^2) in the LiCl electrolyte. A charging current of 0.2 mA was used. Contact resistance was found by taking resistance measurements over varying electrode spacings and extrapolating to zero spacing (Figure S2).[13] The −80 °C measurement was taken after holding for 90 min.

■ RESULTS AND DISCUSSION

Relative to many organic solvents, pure water has a high freezing point of 0 °C. However, the addition of salts and other solvents (i.e., road salt or alcohol) depresses this temperature by several tens of degrees. In an ideal case, freezing point depression is a colligative property: irrespective of the identity of the solute, the freezing point of the solution will proportionally decrease with solute concentration. This simple relationship holds in the dilute limit where the solute species do not interact. Of course, at sufficiently high concentrations, the solute will precipitate at moderately low temperatures, potentially forming an insulating barrier at interfaces. A phase diagram is necessary to capture transitions across a broad concentration range.

Water is an excellent solvent that forms very concentrated solutions of certain salts. Near the solubility limit (∼20 m) of some lithium salts, solutions take on a unique solvation structure and are capable of operating at high voltages.[9] These solutions, called "water in salt" electrolytes, are far more concentrated than conventional electrolytes (∼1 m). The aqueous electrolyte used in this study contains LiCl at an intermediate concentration: the eutectic (6.8 m or 24.8 wt %) where the liquid−solid transition is at its minimum, −74 °C (Figure 1).[11] Incidentally, the conductivity is greatest around this concentration.[12] Below this concentration, ice forms at relatively higher temperatures and, above it, LiCl precipitates. Both transitions are expected to hurt electrolyte performance at low temperatures.[13] Given the high concentration of charge carriers in the eutectic solution and the massively depressed
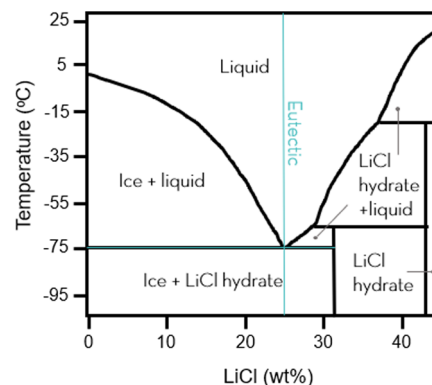

Figure 1. LiCl−H$_2$O phase diagram. At 24.8% LiCl, the solution forms a eutectic with a freezing point of −74 °C.
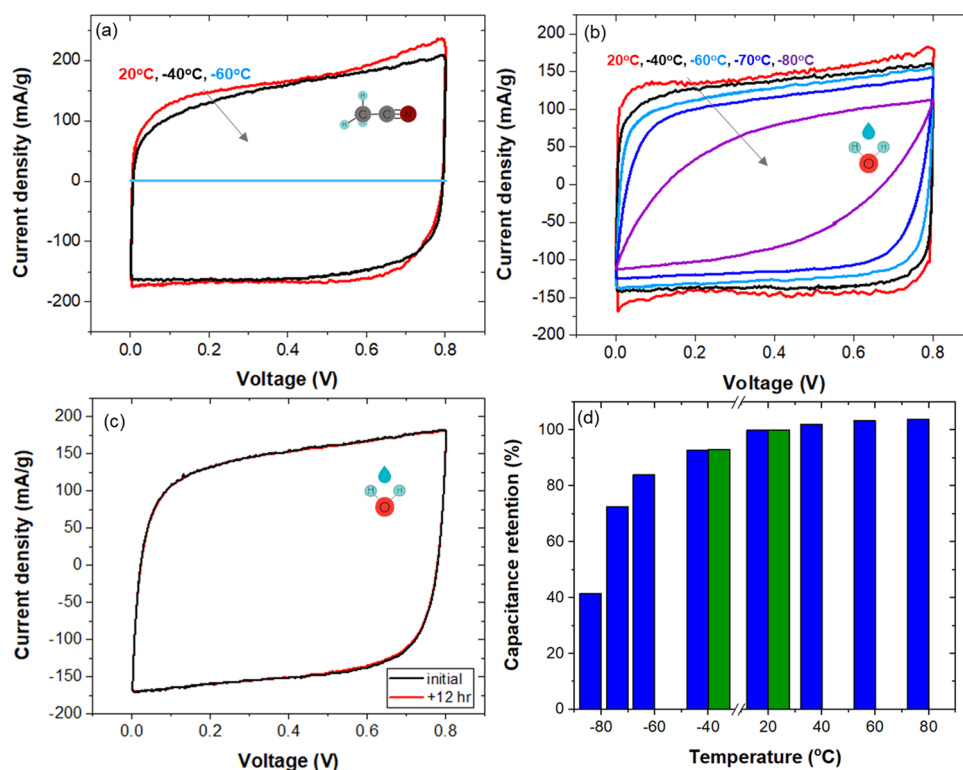
Figure 2. Electrochemical performance at low temperature of conventional and aqueous devices. Cyclic voltammetry (CV) of carbon supercapacitors containing (a) organic (0.5 m TEABF$_4$ in acetonitrile) electrolyte and (b) aqueous eutectic (LiCl 24.8 wt %) electrolyte. Charging was performed at 5 mV/s at different temperatures. (c) CV measurements taken before and after a 12-h hold at −70 °C. (d) Percent capacitance retention across a range of temperatures for the aqueous (blue) and acetonitrile (green) devices.
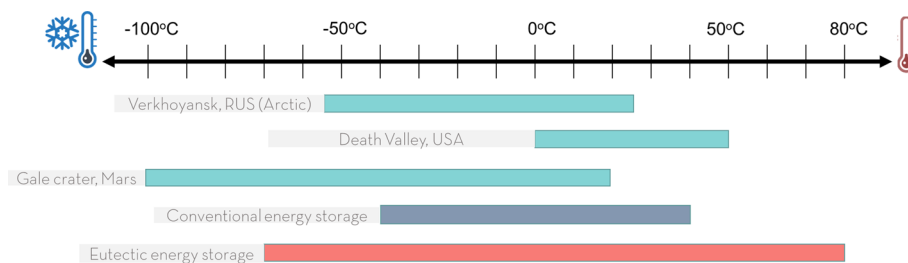

Figure 3. Comparison of the temperature windows of operation for the aqueous eutectic device and conventional energy storage as well as examples of extreme conditions found on Earth and Mars.

freezing point, it is expected to perform as an excellent low-temperature electrolyte.

Energy Storage at Low Temperatures. The eutectic LiCl electrolyte was paired with electrodes coated in an unmodified, commercial activated carbon (Kuraray YP-80FP) to evaluate its performance to support energy storage at low temperatures. Carbon electrodes were used, which eliminate possible corrosive issues in the chloride-containing electrolyte. As a point of comparison, supercapacitors containing a conventional organic electrolyte (0.5 m tetraethylammonium tetrafluoroborate (TEABF$_4$) in acetonitrile) were also subjected to low-temperature testing. Figure 2a,b shows charging cycles (cyclic voltammetry performed at 5 mV/s) at various temperatures of the organic and aqueous device, respectively. The organic electrolyte device performs well down to −40 °C without any significant loss of capacity. At −60 °C, below the freezing point of acetonitrile (−45 °C), charging ceases. The device containing the eutectic LiCl electrolyte performs superbly down to −70 °C, retaining 72%

of the room temperature capacity (28 F/g) and fast charging kinetics evidenced by a square-shaped profile. Energy density versus temperature for the aqueous and organic devices is included in the Supporting Information (Figure S3). Zero low-temperature fatigue for the aqueous device is seen at −70 °C over a 12-h hold, with charging curves taken before and after overlaying almost perfectly (Figure 2c). Surprisingly, the aqueous device even supports substantial charging (42% of room temperature capacity) at −80 °C, below the expected freezing point of the water-based eutectic electrolyte.

Since the aqueous electrolyte is nonflammable, energy storage is also possible at high temperatures - up to 80 °C without any losses (Figure S4). Percent capacitance retained at high and low temperatures (relative to room temperature), is presented in Figure 2d. With a conservative temperature range from −70 to 80 °C, the eutectic LiCl electrolyte can support operation over a very broad 150 °C window. Figure 3 compares the temperature ranges of this aqueous device with conventional energy storage as well as examples of extreme
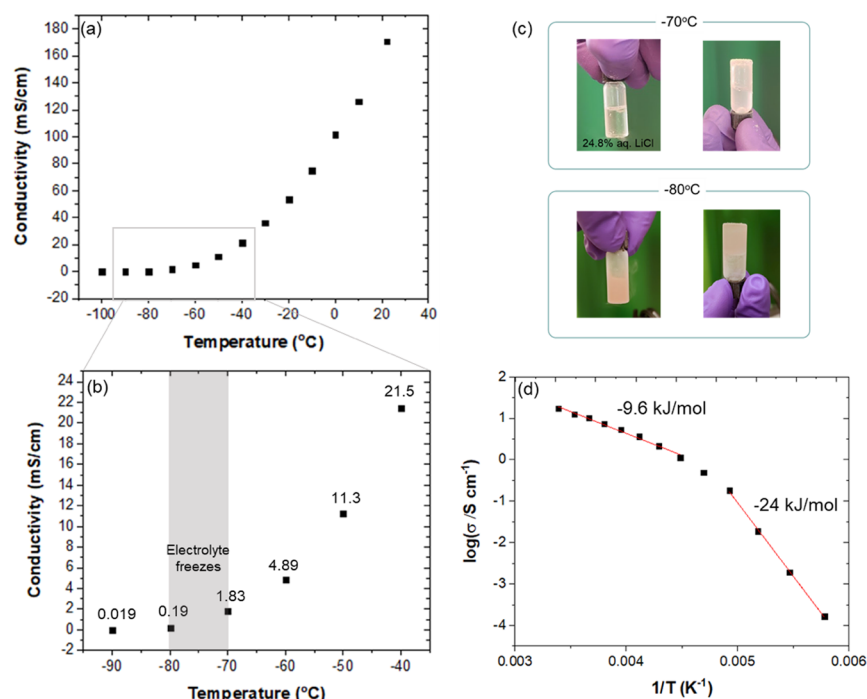
Figure 4. Conductivity of aqueous LiCl eutectic electrolyte at different temperatures. (a) Conductivity versus temperature and (b) magnified low-temperature region with values shown. (c) Photographs of liquid and frozen LiCl electrolyte at −70 and −80 °C. (d) Arrhenius plot of temperature-conductivity data with activation energies is shown.

conditions found on Earth and Mars. The range of the eutectic energy storage easily spans some of the coldest places on earth—a town in the Arctic where temperatures dip below −50 °C—and the hottest—such as Death Valley where temperatures reach 50 °C. The lower limit of this range is close to the coldest temperatures experienced at Gale crater on Mars. Such energy storage would require less heating to stay operational than less efficient, conventional devices.

To look fundamentally at the eutectic LiCl electrolyte and understand the origin of its low-temperature performance, the temperature-dependent conductivity was measured (Figure 4a,b). As expected for an aqueous electrolyte, the conductivity is very high, about 180 mS/cm at room temperature. This is 1−2 orders of magnitude higher than organic electrolytes which typically have a conductivity between 1 and 10 mS/cm.[14] Even when the temperature falls to −70 °C, the eutectic is still quite conductive −1.83 mS/cm which is still in the range of organic electrolytes when measured at room temperature. This remarkable conductivity is largely why the electrolyte performs so well at low temperature—even when paired with an industry-standard, unmodified electrode material. Below this temperature, the electrolyte is visually observed to freeze (Figure 4c) after which the conductivity falls at a much faster rate. When an Arrhenius plot of the conductivity-temperature data is made (Figure 4d), two distinct regions can be visualized. Above the eutectic freezing point, conduction occurs with low activation energy—solvated ions are diffusing in a fluid medium. Below the freezing point, the conduction still occurs but via another mechanism with higher activation energy. Likely, lithium ions are conducting via hopping within a static water network, as was shown theoretically for copper ions in frozen aqueous solutions.[15] Even in this frozen state at −80 °C the electrolyte has a conductivity of 0.19 mS/cm on par with typical solid-state ionic conductors when measured at room temperature.[14,16,17] This mode of conduction is

responsible for the more sluggish yet significant charge storage seen earlier at −80 °C. Recently, others have observed aqueous proton batteries operating below the freezing point of the constituent acidic electrolytes.[18,19] Here, we specifically find that proton conduction (perhaps by the Grotthuss mechanism) is not necessary to enable exceptionally high ionic conductivities and energy storage even in frozen aqueous solutions.[19]

Clearly, aqueous electrolytes possess distinct advantages over typical organic electrolytes for energy storage applications in cold environments. A high baseline conductivity supports ionic currents at low temperatures and the unique hydrogen bonding of water solubilizes large fractions of lithium chloride, allowing for a massive freezing point depression. Still, the small electrochemical stability window of aqueous electrolytes relative to organic generally precludes their adoption into commercial energy storage devices. In the low-temperature case, however, the rates of solvent decomposition (hydrogen and oxygen evolution) are expected to be significantly lowered since these are activation-limited processes (the reactant is the solvent). Figure 5 shows the electrochemical stability windows of the 24.8% LiCl solution at room temperature, −40 °C, and −70 °C, evaluated with linear sweep voltammetry on a platinum working electrode. From room temperature to −70 °C, the stability window of the aqueous electrolyte expands by 1 V. The voltage window reaches 3 V at −70 °C, within the range of common organic electrolytes. This is a sensible result. Given that hydrogen and oxygen evolution are activation-limited, the reaction rate constants should exhibit a very strong (logarithmic) dependence on temperature as they obey the Arrhenius equation. Furthermore, the dissociation constant of water is reduced at low temperatures, limiting the concentrations of H+ and OH− which participate in the electrolysis reaction.[20] The result is that the eutectic LiCl electrolyte can support a high-rate energy storage at low temperatures
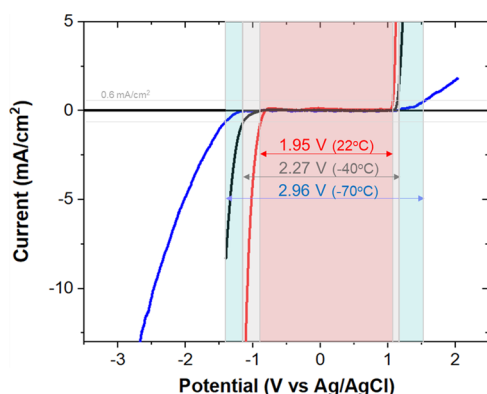
Figure 5. Electrochemical stability of aqueous LiCl eutectic at different temperatures. Measurements were taken with linear sweep voltammetry at 10 mV/s on a platinum working electrode with a Ag/AgCl reference.

exceedingly well. Indeed, this aqueous electrolyte behaves at low temperature—with high conductivity and a wide stability window—like a typical organic electrolyte at room temperature.

Low-Temperature Polymer Electrolyte. While liquid electrolytes offer the highest conductivities, there are a lot of incentives to develop polymer electrolytes: adopting a leak-free, flexible, low-volatile gel material in place of a liquid could streamline both device design and manufacturing. For these reasons, we sought to translate the low-temperature performance of the liquid LiCl eutectic to a solid polymer electrolyte.

A mixture of aqueous LiCl and poly(vinyl alcohol)—another very low-cost, nontoxic material—was used as a gel electrolyte in the same energy storage device as above and subjected to low-temperature charging characterizations. This polymer electrolyte enables energy storage down to −70 °C, though less efficiently than the liquid electrolyte (Figure 6a). The slower charging rates are compensated for with the greatly expanded voltage window at low temperatures (Figure 6b): at −70 °C, the voltage window for the polymer gel device is at least 2.2 V, translating to an energy density three times that of room temperature. In this sense, these devices actually perform better at low temperatures. Cycling at −70 °C shows zero fatigue over 1000 cycles, demonstrating that charge storage is reversible at low temperatures (Figure 6c). High-temperature cycling at 80 °C shows similar results (Figure S5). A larger scale pouch cell was made, which is shown in Figure 6d. At −70 °C, it can deliver enough power to light a yellow light emitting diode (LED) for more than a minute (supporting video).

◼ CONCLUSIONS

In this work, we demonstrate the remarkable performance of concentrated aqueous electrolytes for low-temperature energy storage. A eutectic mixture of lithium chloride, a commodity chemical, and water remains liquid down to −74 °C. This electrolyte possesses a remarkably high conductivity of 1.83 mS/cm at −70 °C, which is in the range of typical organic electrolytes when measured at room temperature. Such a high conductivity easily enables low-temperature energy storage in
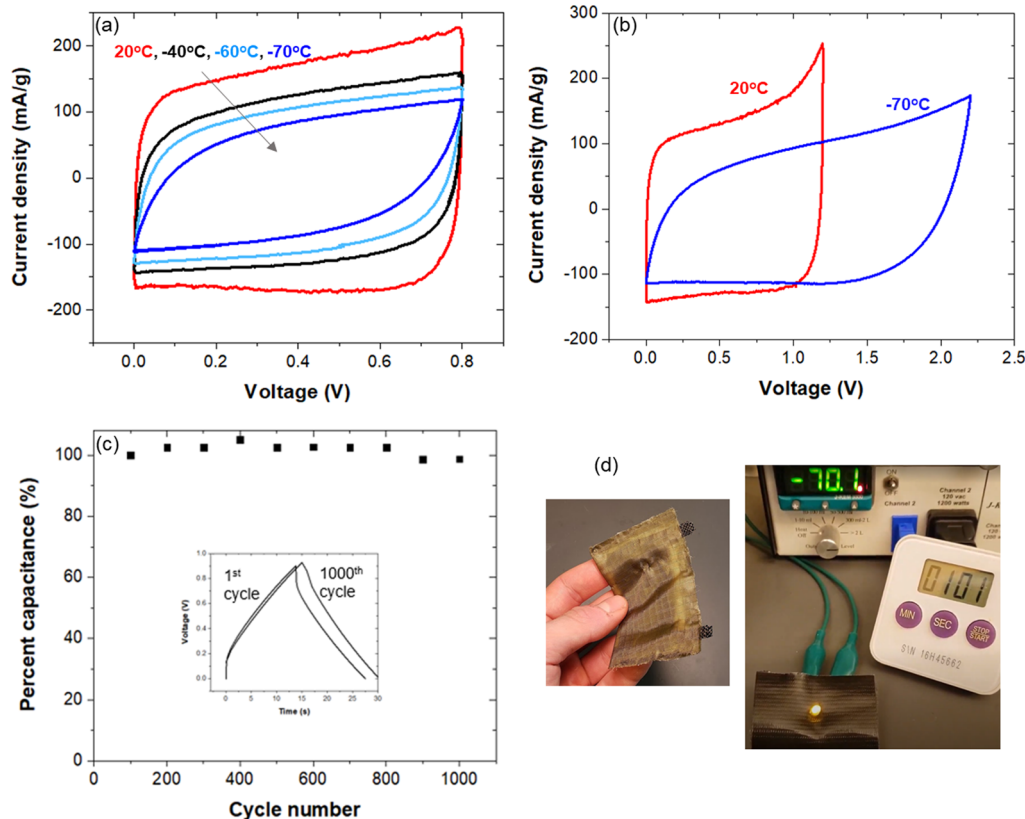

Figure 6. Low-temperature characterizations of an energy storage device containing a LiCl gel electrolyte. (a) CV charging of the device down to −70 °C. (b) Voltage window expansion at −70 °C relative to 20 °C. (c) 1000 charge−discharge cycles with an applied constant current of 1 A/g at −70 °C. (d) Large-scale device powering a yellow LED at −70 °C.

supercapacitors containing a completely unmodified, industry-standard activated carbon. In such devices, 72% of room temperature capacitance (28 F/g) is maintained at −70 °C and, incidentally, the stability window of the electrolyte is greatly widened to 3 V. Clearly, the advantage of aqueous electrolytes—high ionic conductivity—is exemplified at low temperature, while the primary disadvantage—narrow stability window—is mitigated, making aqueous electrolytes an unexpected yet ideal candidate for low-temperature applications. A mixture of PVA and aqueous LiCl forms a gel electrolyte which retains much of the low-temperature properties of the liquid eutectic and can support powering an LED at −70 °C. The energy storage system presented here can easily operate in the most extreme conditions found on earth and does so using only low-cost, commercial, and environmentally benign materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09676.

> Low-temperature measurement chamber; contact resistance measurements; energy density versus temperature; high-temperature operation of an activated carbon supercapacitor; and high-temperature cycling characterization (PDF)
>
> Video showing a yellow LED powered by the aqueous electrolyte stored at −70 °C for more than a minute (MP4)

■ AUTHOR INFORMATION

Corresponding Author

> **Trisha L. Andrew** − *Department of Chemical Engineering and Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States;* Ⓞ orcid.org/0000-0002-8193-2912; Email: tandrew@umass.edu

Author

> **Wesley Viola** − *Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpcc.0c09676

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Reyes, J. R. M. D.; Parsons, R. V.; Hoemsen, R. Winter happens: The effect of ambient temperature on the travel range of electric vehicles. *IEEE Trans. on Vehicular Technol.* **2016**, *65*, 4016−4022.

(2) Iwama, E.; Taberna, P. L.; Azais, P.; Brégeon, L.; Simon, P. Characterization of commercial supercapacitors for low temperature applications. *J. Power Sources* **2012**, *219*, 235−239.

(3) Brandon, E. J.; West, W. C.; Smart, M. C.; Whitcanack, L. D.; Plett, G. A. Extending the low temperature operational limit of double-layer capacitors. *J. Power Sources* **2007**, *170*, 225−232.

(4) Xu, J.; Yuan, N.; Razal, J. M.; Zheng, Y.; Zhou, X.; Ding, J.; Cho, K.; Ge, S.; Zhang, R.; Gogotsi, Y.; Baughman, R. H. Temperature-independent capacitance of carbon-based supercapacitor from −100 to 60 C. *Energy Storage Mater.* **2019**, *22*, 323−329.

(5) West, W. C.; Smart, M. C.; Brandon, E. J.; Whitcanack, L. D.; Plett, G. A. Double-layer capacitor electrolytes using 1, 3-Dioxolane for low temperature operation. *J. Electrochem. Soc.* **2008**, *155*, A716−A720.

(6) Tsai, W. Y.; Lin, R.; Murali, S.; Zhang, L. L.; McDonough, J. K.; Ruoff, R. S.; Taberna, P. L.; Gogotsi, Y.; Simon, P. Outstanding performance of activated graphene based supercapacitors in ionic liquid electrolyte from −50 to 80 C. *Nano Energy* **2013**, *2*, 403−411.

(7) Lin, R.; Taberna, P. L.; Fantini, S.; Presser, V.; Pérez, C. R.; Malbosc, F.; Rupesinghe, N. L.; Teo, K. B.; Gogotsi, Y.; Simon, P. Capacitive energy storage from −50 to 100 C using an ionic liquid electrolyte. *J. Phys. Chem. Lett.* **2011**, *2*, 2396−2401.

(8) Zhang, C.; Zhang, L.; Yu, G. Eutectic electrolytes as a promising platform for next-generation electrochemical energy storage. *Acc. Chem. Res.* **2020**, *53*, 1648−1659.

(9) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. Water-in-salt electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **2015**, *350*, 938−943.

(10) Bu, X.; Zhang, Y.; Sun, Y.; Su, L.; Meng, J.; Lu, X.; Yan, X. NAll-climate aqueous supercapacitor enabled by a deep eutectic solvent electrolyte based on salt hydrate. *J. Energy Chem.* **2020**, *49*, 198−204.

(11) Monnin, C.; Dubois, M.; Papaiconomou, N.; Simonin, J. P. Thermodynamics of the LiCl+H2O system. *J. Chem. Eng. Data* **2002**, *47*, 1331−1336.

(12) Yim, C. H.; Abu-Lebdeh, Y. A. Connection between phase diagram, structure and ion transport in liquid, aqueous electrolyte solutions of Lithium chloride. *J. Electrochem. Soc.* **2018**, *165*, A547.

(13) Ramanujapuram, A.; Yushin, G. Understanding the Exceptional Performance of Lithium-Ion Battery Cathodes in Aqueous Electrolytes at Subzero Temperatures. *Adv. Energy Mater.* **2018**, *8*, 1802624.

(14) Marcinek, M.; Syzdek, J.; Marczewski, M.; Piszcz, M.; Niedzicki, L.; Kalita, M.; Plewa-Marczewska, A.; Bitner, A.; Wieczorek, P.; Trzeciak, T.; Kasprzyk, M. Electrolytes for Li-ion transport−Review. *Solid State Ionics* **2015**, *276*, 107−126.

(15) Guo, Z.; Wang, T.; Wei, H.; Long, Y.; Yang, C.; Wang, D.; Lang, J.; Huang, K.; Hussain, N.; Song, C.; Guan, B. Ice as solid electrolyte to conduct various kinds of ions. *Am. Ethnol.* **2019**, *58*, 12569−12573.

(16) Zhang, W.; Nie, J.; Li, F.; Wang, Z. L.; Sun, C. A durable and safe solid-state lithium battery with a hybrid electrolyte membrane. *Nano Energy* **2018**, *45*, 413−419.

(17) Thangadurai, V.; Narayanan, S.; Pinzaru, D. Garnet-type solid-state fast Li ion conductors for Li batteries: critical review. *Chem. Soc. Rev.* **2014**, *43*, 4714−4727.

(18) Yan, L.; Huang, J.; Guo, Z.; Dong, X.; Wang, Z.; Wang, Y. Solid-State Proton Battery Operated at Ultralow Temperature. *ACS Energy Lett.* **2020**, *5*, 685−691.

(19) Jiang, H.; Shin, W.; Ma, L.; Hong, J. J.; Wei, Z.; Liu, Y.; Zhang, S.; Wu, X.; Xu, Y.; Guo, Q.; Subramanian, M. A. A High-Rate Aqueous Proton Battery Delivering Power Below −78° C via an Unfrozen Phosphoric Acid. *Adv. Energy Mater.* **2020**, *10*, 2000968.

(20) Verma, M.P.; A thermodynamic assessment of dissociation constant of water. *In Proceedings 28th workshop on geothermal reservoir engineering*, 2003.