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A comprehensive formulation of green aqueous electrolytes while enabling low temperature operations

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Safer-by-design and sustainable energy storage devices are envisioned as among the required 2.0 solutions to satisfy the fast-growing energy demands. Responding to this evolution cannot be freed from a global and synergetic approach to design the requisite electrolytes taking into account the toxicity, the eco-compatibility and the cost of their constituents. An unprecedented strategy was performed targeting low temperature applications, a non-toxic and cost-efficient eutectic system LiNO₃ in water with 1,3-propylene glycol as co-solvent was concomitantly selected to design a ternary electrolyte with a wide liquid range. By using this electrolyte in an electrostatic double-layer capacitor (EDLC), the operating voltage of the device reaches an optimum of 2.0 V at -40 °C over more than 100 h of floating. Moreover, after being set up at 20 °C, the temperature resilience of the capacitance is near total, demonstrating thus a promising feature related to the suitable thermal and electrochemical behaviours of the tested EDLC devices.

Introduction

The development of efficient energy storage technologies is the key for reaching a sustainable energy future. Electrochemical energy storage systems, such as batteries or supercapacitors, can be considered as the best alternatives for energy storage. Among the various existing systems, due to high power density, supercapacitors have gained strong interest with the aim of increasing its energy density remaining as the principal limit for decades. As a solution, the potential window extension was provided by the formulation of highly concentrated aqueous electrolytes, due to the reduction of free water molecules.¹⁻³ Furthermore this strategy was extended to low-temperature applications with a mitigated success.⁴⁻⁵ Historically, conventional electrostatic double-layer capacitors (EDLCs) organic electrolytes were ideally suitable for low-temperature applications, acetonitrile (ACN) based electrolytes can operate at -40 °C without any changes in the formulation.⁶ Such devices exhibit regular capacitances ($\approx 25 \text{ F}\cdot\text{g}^{-1}$ at 20 °C and $15 \text{ F}\cdot\text{g}^{-1}$ at -40 °C) on an operating voltage up to 2.0 V. Due to low crystallization point of most of organic solvents (esters, cyclic ethers or nitriles), this class of chemicals are used, as co-solvents, for decreasing the operating temperature of common supercapacitors.⁷ 1,3-dioxalane, added to the commercial

system (ACN + Et₄NBF₄) allows cycling at least at -70 °C.^{7,8} The resulting capacitance is $12.4 \text{ F}\cdot\text{g}^{-1}$ at -70 °C for 2.5 V operating voltage. These interesting performances are obtained thanks to intrinsic low viscosity solvents unfortunately associated to a certain toxicity. Consequently, propylene carbonate (PC) was substituted to ACN since its vapour pressure and acute toxicity are lower.⁹⁻¹¹

As alternatives to organic solvents, ionic-liquid-based electrolytes exhibit crystallization below -40 °C but are accompanied by drastic loss of performances due to the important increase of viscosity, consequently these electrolytes will be no further considered by using solely pure ionic liquids.¹² However, due to more constraining safety policies, intrinsic properties, such as cost, safety and toxicity, overcame the energy density as limits to solve. The flammability, and the associated toxicity and environmental hazard, of current organic based electrolytes (*i.e.* toxic solvent like ACN) are certainly the most critical issues in terms of safety.

Among the different solutions, such as polymer and/or inorganic solid electrolytes, the best strategy consists in using aqueous electrolytes. Current trendy investigations are electrochemical storage systems operating at low temperature for crucial applications which represents an immense challenge for aqueous electrolytes due to crystallization point of water. Despite a limited operating voltage leading to lower energy density, the non-flammability of water-based electrolytes is an tremendous benefit.^{13,14} Moreover, aqueous electrolytes are commonly based on nitrate or sulfate salts which considerably reduce their cost,^{15,16} and contrariwise of organic solvents, aqueous solution exhibits high ionic conductivity.¹⁴ Considering their safety, sustainability and low economic impact, aqueous electrolytes perfectly fit into current environmental and economic critical challenges. However, improvement in terms of energy density is still required and the electrochemical stability window of water-based electrolytes, limited to 1.23 V due to decomposition into O₂ and H₂, remains the main problem to be faced. Several studies showed that the improvement of operating potential window is possible by suppressing dissolution of current collector and increasing the solvent stability.¹⁷⁻¹⁹ Moreover, a previous study showed that designing a

binary aqueous electrolyte at a specific composition (concentrated eutectic) led to a device able to cycle at relative low temperature (limited to T_E , eutectic melting temperature) with widened potential window.²⁰ Despite a non-negligible improvement in term of cost and eco-toxicity, such aqueous electrolyte remains limited to an operating temperature of $-25\text{ }^\circ\text{C}$ and an intermediate potential window ($\approx 2.2\text{ V}$), compared to organic-based supercapacitors.

As a solution, few studies are performed on water-based electrolytes by preparing ternary systems using a co-solvent lowering the crystallization temperature. The first examples of mixed solvents are coming from the previous binary electrolytes and are based on the combination of ACN and H_2O with different salts for battery or supercapacitor applications.^{21,22} Concerning the latter, the mixture of LiTFSI/ H_2O /ACN (1/2.6/2.3; molar ratio) allows to go down to $-30\text{ }^\circ\text{C}$ with an operating voltage of 2.2 V to reach $22\text{ F}\cdot\text{g}^{-1}$ at $1\text{ A}\cdot\text{g}^{-1}$ but falling to $8.6\text{ F}\cdot\text{g}^{-1}$ at $10\text{ A}\cdot\text{g}^{-1}$ on activated carbon electrodes.²³ Switching from LiTFSI to NaClO_4 , Yan *et al.* achieved to operate a supercapacitor down to $-50\text{ }^\circ\text{C}$ with $27.5\text{ F}\cdot\text{g}^{-1}$ at $20\text{ mV}\cdot\text{s}^{-1}$ with a potential window of 2.3 V .²⁴ In replacement of ACN, dimethylsulfoxide (DMSO) was used with water (1:2) with 6.6 m of LiTFSI. This ternary electrolyte exhibits a potential window of 3 V and could cycle down to $-35\text{ }^\circ\text{C}$ but with a significant capacitance drop from $68\text{ F}\cdot\text{g}^{-1}$ at $25\text{ }^\circ\text{C}$ to $21\text{ F}\cdot\text{g}^{-1}$ at $-35\text{ }^\circ\text{C}$ with a specific current of $1\text{ A}\cdot\text{g}^{-1}$.²⁵ Béguin *et al.* proposed an alternative, they prepared Li_2SO_4 0.7 M in 7:3 vol:vol water/methanol mixture as electrolyte for symmetric A.C./A.C. supercapacitor operating at $-40\text{ }^\circ\text{C}$ with an remarkable floating stability and a capacitance of $19\text{ F}\cdot\text{g}^{-1}$ at 1.6 V .²⁶

These described works have enabled notable advances in terms of performance, operating temperatures and voltages. However, in any cases, safety, toxicity toward human and/or environment were concomitantly taken as a primary parameter for the design of the electrolyte. Herein is proposed a method combining the emphasis on these parameters while keeping performance objectives at low temperatures.

Results and Discussion

To begin with, it is interesting to dive back into the hazards, the toxicity and the eco-compatibility of the most well-known components of aqueous ternary electrolytic mixtures based on lithium salts following the guidelines of the REACH program (Registration, Evaluation and Authorization of Chemicals), especially the first and main objective which corresponds to the protection of human health and the environment. In aqueous electrolytes, salts play a special role, and the candidates are few. The most common are gathered in Table 1 with their melting and decomposition temperatures as well as their median lethal dose (LD_{50}) accompanied by their NFPA 704 and GSH classifications. At first, LiTFSI, which many consider to be a promising salt in concentrated aqueous electrolytes, appears to be in difficulty here because of its corrosiveness and its acute and long-term toxicity.³² The only positive point of LiTFSI is that it is not acting as an oxidizer in combination with an organic solvent, usually flammable. Finally, recent studies have shown that this salt is not the most suitable for obtaining low-temperature operating electrolytes and is therefore excluded for this study.^{4,20}

In a second time, LiClO_4 , although it having adequate physico-chemical properties, nevertheless, it remains a strong oxidizer and is considered hazardous for health. Indeed, even if there is no precise data on LiClO_4 , other perchlorates are considered potentially carcinogenic.³⁴ Lithium sulfate (Li_2SO_4) appears to be an interesting possibility given that it is not considered as an oxidizer and is a stable compound up to $859\text{ }^\circ\text{C}$. It is only categorized as an eye irritating agent, has a moderate oral toxicity (LD_{50} : $0.613\text{ g}\cdot\text{kg}^{-1}$) and is not harmful to the environment. However, its bivalent anion leads to a lower solubility in water ($349\text{ g}\cdot\text{dm}^{-3}$ vs. $900\text{ g}\cdot\text{dm}^{-3}$ for LiNO_3) dropping its interest to diminish the amount of free water.^{28,35} It is therefore a viable salt for a safer and greener approach of low-concentration electrolytes. Finally, LiNO_3 , although it is a well-known salt with a reduce stability at high temperatures, has a very low toxicity to both health and environment, which places it as a top choice in the context of our study.^{27,28}

Table 1 Key parameters of hazards, toxicity and eco-compatibility of most common lithium salts.

| Salt | CAS N° | T_m ($^\circ\text{C}$) | $T_{\text{Decomposition}}$ ($^\circ\text{C}$) | LD_{50} ($\text{g}\cdot\text{kg}^{-1}$) | NFPA 704 | GSH | References |
|--------------------------|------------|----------------------------|---|--|----------|-----|------------|
| LiNO_3 | 7790-69-4 | 264 | 540-740 | 1.426 | | | [27], [28] |
| Li_2SO_4 | 10377-48-7 | 859 | / | 0.613 | | | [28], [29] |
| LiClO_4 | 7791-03-9 | 247 | ≈ 400 | N.D. | | | [30], [31] |
| LiTFSI | 90076-65-6 | 233 | 340 | 0.160 | N.D. | | [32], [33] |

Following the previous analysis on salts, same process was applied to common water-miscible solvents for ternary electrolytes (Table 2), with their room-temperature vapor pressures, flash points, explosive limits in air, LD₅₀ (corresponding to acute toxicity, *i.e.* not long term toxicity), and NFPA 704 and GSH classifications.

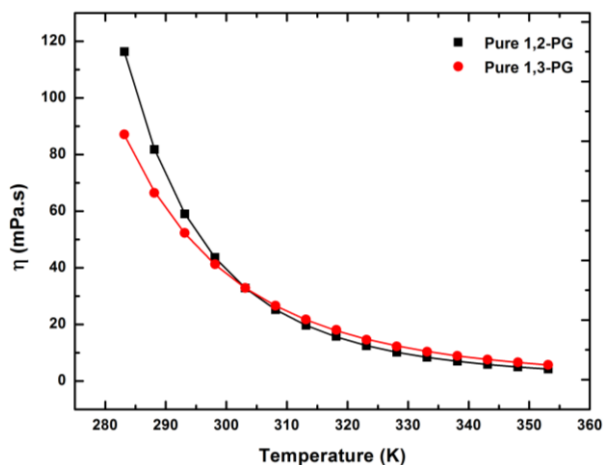
Because of their phase diagrams with water and the presence of a eutectic, MeCN or ACN, and DMSO are intrinsically interesting compounds to formulate aqueous electrolytes for low temperatures.^{55,56} The ACN-water mixture has a eutectic at -10 °C, by adding a significant amount of salt, this value will decrease further due to the reduction in number of free water molecules. These ternary ACN-water-salt mixtures have been and are still studied today, however the majority are with salts that we have previously rejected because of their hazards and toxicity against health and/or environment.²²⁻²⁴ In addition, although ACN is mixed with water, it remains a highly flammable solvent considered dangerous to health, which is in conflict with our approach toward a safer electrolyte.^{50,51} The same conclusions can be taken from the use of DMSO in DMSO-water-salt ternary mixtures. These mixtures showed impressive properties but with salts unsuitable for our study.^{21,25} The main difference is located between flammability and toxicity, DMSO unlike ACN, does not lead to flammable mixtures, but has a greater toxicity. The latter was only demonstrated lately, and is still little taken into account.^{57,58} Another approach to low-temperature ternary electrolytes is based on alcohol-water mixtures because of their ability to form hydrogen bonds with

water. The best known of these is ethylene glycol, which is found in many antifreeze formulations, but it is far too toxic to be considered in our study.⁵⁹ This one is focused on two mono-alcohol, methanol and ethanol, and two isomers of a diol, the 1,2-propylene glycol (1,2-PG) and the 1,3-propylene glycol (1,3-PG). For ethanol and methanol, ignitability is the first obstacle, the flash points are respectively 13 °C and 9 °C illustrating the highly flammable behaviour of these compounds. For methanol, it is necessary to add an acute toxicity by ingestion and inhalation.⁴⁵ Regarding the diols the flammability issues are much more restricted with flash points at 79 °C for 1,3-PG and 99 °C for 1,2-PG. Their respective toxicities are also much lower, only the 1,3-PG is classified as slightly hazardous while the 1,2-PG is considered safe and is the main component of electronic-cigarette liquids.⁶⁰⁻⁶² Therefore, these two diols offer sufficient advantages in terms of safety to select them with LiNO₃ in order to identify a PG-H₂O-LiNO₃ formulation toward a safer and greener low-temperature electrolyte.

As explained previously, 1,2-propylene glycol and 1,3-propylene glycol were identified as solvents perfectly fitting with the current environmental policies and challenges in order to develop greener energy storage systems. However, as a part of an electrolyte, the solvent should also fill some criteria. As a result, the selection between the two glycols was purely based on the viscosity (Fig. 1) which is also an intrinsic relevant (inversely correlated) indicator of the ionic conductivity level. The viscosity values were adjusted by applying the conventional VTF equation

Table 2 Key parameters of hazards, toxicity and eco-compatibility of common water co-solvents for electrolytes.

| Solvent | CAS N° | Vapor pressure (mbar at 25 °C) | Flash point (°C) | Explosive limits in air (%) | LD ₅₀ (g·kg ⁻¹) | NFPA 704 | GSH | References |
|---------|----------|--------------------------------|------------------|-----------------------------|--|----------|-----|------------------------|
| 1,2-PG | 57-55-6 | 0.493 | 99 | 2.6-12.6 | 10-30 | | | [36], [37], [38], [39] |
| 1,3-PG | 504-63-2 | 0.059 | 79 | 2.6(-) | 4.8 | | | [39], [40], [41], [42] |
| MeOH | 67-56-1 | 165.046 | 9 | 6.7-36 | 9.8-13 | | | [43], [44], [45] |
| EtOH | 64-17-5 | 78.730 | 13 | 3.3-19 | 2-7.5 | | | [44], [46], [47] |
| MeCN | 75-05-8 | 91.820 | 6 | 3-16 | 0.2-4 | | | [48], [49], [50], [51] |
| DMSO | 67-68-5 | 0.556 | 95 | 1.8(-) | 2.5-19.7 | | | [39], [52], [53], [54] |



| Name | mp (°C) | bp (°C) | η (25 °C) |
|--------|---------|---------|----------------|
| ACN | -46 | 82 | 0.35 |
| PC | -48.8 | 242 | 2.53 |
| DMSO | 18.5 | 181 | 1.90 |
| MeOH | -98 | 65 | 0.55 |
| EtOH | -114 | 79 | 1.20 |
| 1,2-PG | -59 | 188 | 43.7 |
| 1,3-PG | -26 | 213 | 41.3 |

Figure 1 Viscosities of pure 1,2-PG and 1,3-PG function of temperature along with a table of melting and boiling points of various solvents and their dynamic viscosity (mPa.s).

based on the following equation:

$$\eta = \eta_0 \exp\left(\frac{-B_\eta}{T-T_0}\right) \quad (1)$$

with B_η , η_0 and T_0 adjustable parameters, reported in Table S1 of the ESI.

By extrapolating the fitting parameters, the viscosity at low temperatures can be then extrapolated. At -40 °C, pure 1,2-PG is ten times more viscous ($34.9 \cdot 10^3$ mPa.s) than pure 1,3-PG ($3.6 \cdot 10^3$ mPa.s). As a result, 1,3-PG was selected therein as the co-solvent for designing our ternary electrolyte operating at low temperatures.

Differential Scanning Calorimetry

First, DSC was performed in order to highlight the liquid range of each composition and compared to the binary eutectic LiNO_3 -based electrolyte. First of all, the thermogram of the binary LiNO_3 electrolyte (Fig. 2, black curve) confirms that the eutectic composition is well reached. According to the phase diagram,⁶³ the single crystallization peak and the single melting point around -23 °C are representative of the eutectic composition.

For the first strategy, 24.5 % of LiNO_3 was dissolved in a solvent mixture (H_2O :1,3-PG) with different ratios. The corresponding thermograms (Fig. 2.a.) show that the addition of propylene glycol onto the eutectic binary composition completely disturbed its thermal behavior. This is visualized by the appearance of several crystallization peaks. As suspected a ratio (low in 1,3-PG, ≤ 10 %) of solvents is closed to eutectic binary system while reaching a ratio containing more than 10 % of propylene glycol totally affected the eutectic behaviour. However, for the specific ratio of 75:25 (water:1,3-PG) (Fig. 2.a., pink curve), the crystallization did not occur highlighting the possible presence of a eutectic point below -60 °C or at least a liquid range suitable to the targeted supercapacitor specifications (-40 to 60 °C). A second approach consisted of the addition of 1,3-PG in the binary system (eutectic LiNO_3). Based on the first approach and the search of the widest liquid range, only the heating curves are presented (Fig. 2.b.). From 1 to 15 %, the liquidus temperature is shifted from -12.2 °C to nearly the eutectic temperature around -23 °C. Furthermore, reaching 18 wt.% of added 1,3-PG, the disappearance of the melting peak, e.g. no crystallization peak, highlighted that this composition is liquid on the targeted temperature range.

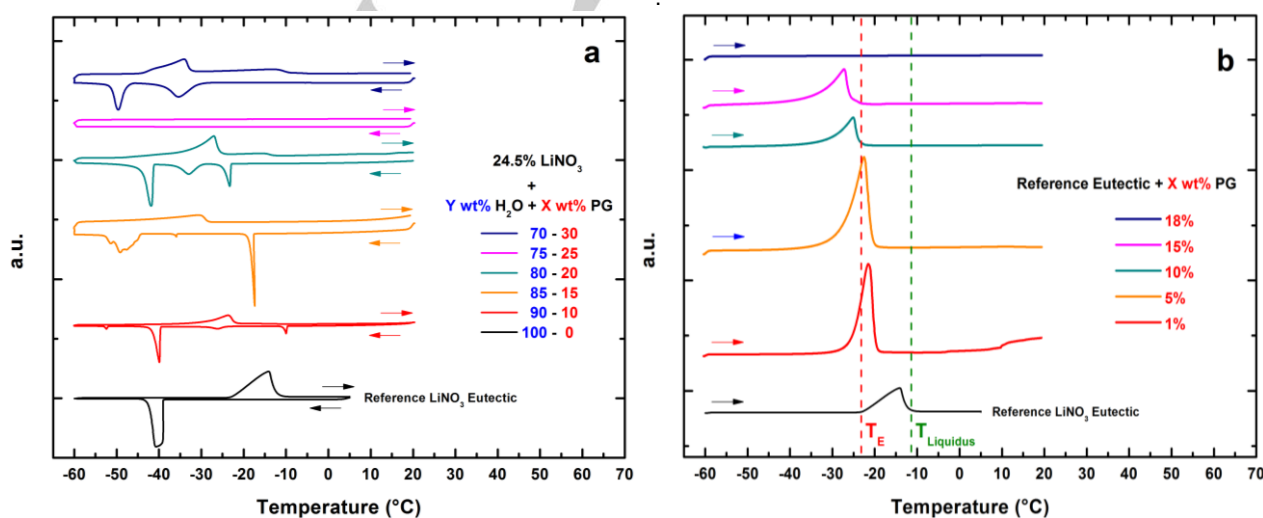
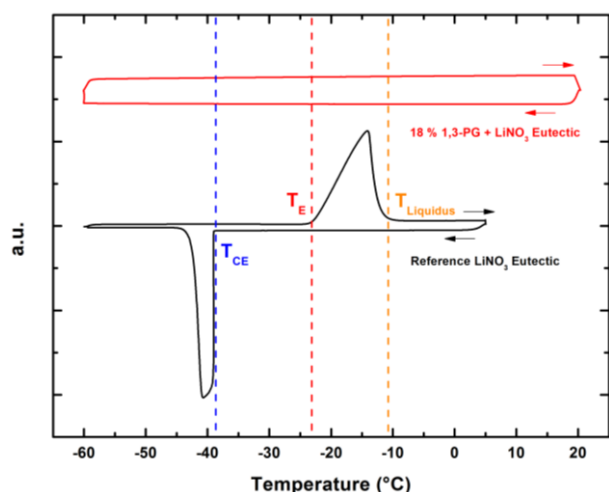
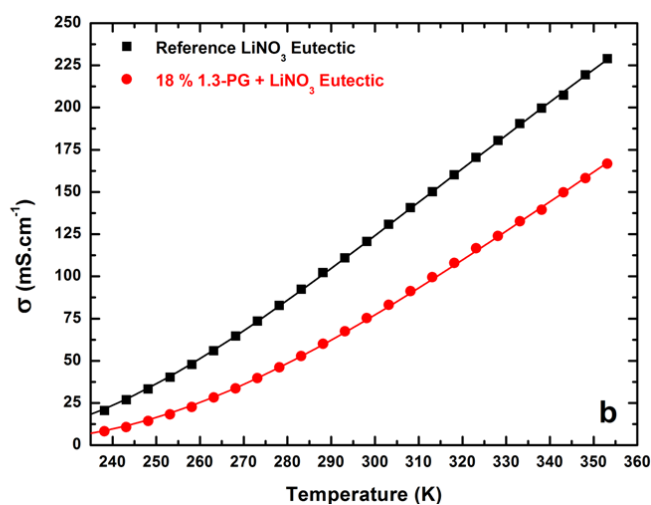
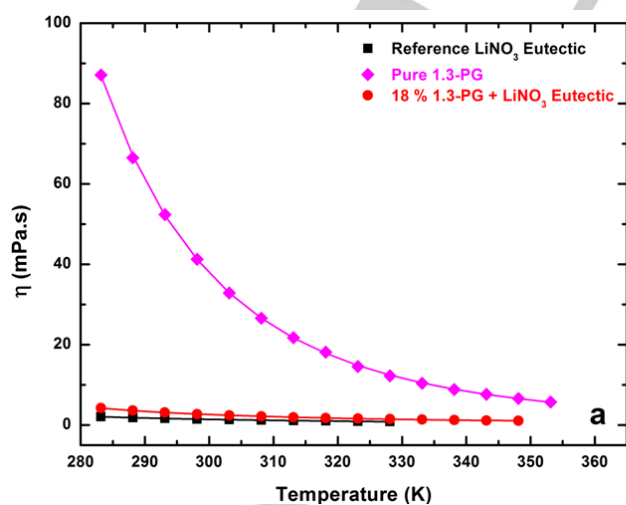


Figure 2 (a) Thermograms of different compositions based on strategy 1 – 24.5 % in mass of LiNO_3 in several PG: H_2O ratios and (b) thermograms of different compositions based on strategy 2 – Addition of different quantities of PG in binary LiNO_3 : H_2O eutectic.

Table 3 Molar and mass composition of the two electrolytes selected from strategies 1 and 2.

| Sample | Composition | | | | | |
|---|-------------------|-------|------------------|-------|---------|-------|
| | LiNO ₃ | | H ₂ O | | 1,3-PG | |
| | x mol.% | wt. % | x mol.% | wt. % | x mol.% | wt. % |
| 24.5 % LiNO ₃ + water:PG (75:25) | 9.48 | 24.50 | 83.91 | 56.63 | 6.61 | 18.87 |
| 18 % 1,3-PG + LiNO ₃ eutectic | 7.30 | 20.09 | 86.16 | 61.91 | 6.54 | 18.00 |

According to the table 3, the two electrolytes, liquid between -60 and 40 °C, are of approximately the same composition and specifically in term of propylene content. As a result, it is impossible to affirm that a eutectic point is reached but the liquid behaviour, over the target temperature range,⁶⁴ of such compositions make them as the ideal candidate for supercapacitors. The composition, LiNO₃ eutectic + 18 wt. % 1,3-PG, was then fully investigated. First of all, the thermogram is depicted in Fig. 3. It confirms, by the absence of any peak, the liquid behaviour of this electrolyte on the studied temperatures.

**Figure 3** Thermograms of the reference (LiNO₃ eutectic) and 18 % 1,3-PG + LiNO₃ eutectic.**Figure 4** (a) Viscosity of pure 1,3-PG, the reference (LiNO₃ eutectic) and 18 % 1,3-PG + LiNO₃ eutectic and (b) Conductivity of the reference (LiNO₃ eutectic) and 18 % 1,3-PG + LiNO₃ eutectic.

As preview of electrochemical performances, the investigation of transport properties (viscosity and conductivity) was performed. Moreover, the interest of the eutectic composition, compared to other concentrations, is reminded in Fig. S1 of the ESI.

First of all, viscosities were measured, as function of temperature, for the binary eutectic electrolyte (reference), and the ternary mixture. The results are given in Fig. 4.a. The viscosity of the binary mixture is in agreement with literature for such concentration.⁶⁵ Regarding pure propylene glycol, the viscosity is 10 times higher than aqueous solution at 25 °C. However, its addition (18 % in mass) in the eutectic mixture only doubled the viscosity (3.13 mPa.s against 1.65 mPa.s). The viscosity values were adjusted by applying the conventional VTF equation and B_η , η_0 and T_0 adjustable parameters are reported in Table S1 of the ESI.

The conductivity of the ternary mixture was measured as function of the temperature from -40 to 80 °C and is compared to the binary eutectic composition as reference. The resulting curves are plotted in Fig. 4.b.

The temperature dependence of the two electrolytes is fitted using VTF equation reported below:

$$\sigma = \sigma_0 \exp \quad (2)$$

With B_σ , σ_0 and T_0 adjustable parameters, reported in Table S1 of the ESI.

The ternary electrolyte, compared to the reference, undergoes a drop of conductivity, consequence of the addition of propylene glycol and its viscosity leading to a decrease of ionic mobility. By looking in depth at the data collected in Table 4, this viscosity, induced by the 1,3-PG and the high concentration of LiNO₃ (3.65 m), has only a moderate impact on transport properties. The ionic conductivity of the described electrolyte (67.5 mS.cm⁻¹) remains very close to that of aqueous binary electrolytes while its viscosity is closer to carbonate-based organic electrolytes.

Table 4 Viscosity and conductivity of 18 % PG + LiNO₃ eutectic compared to classic aqueous and organic electrolytes.

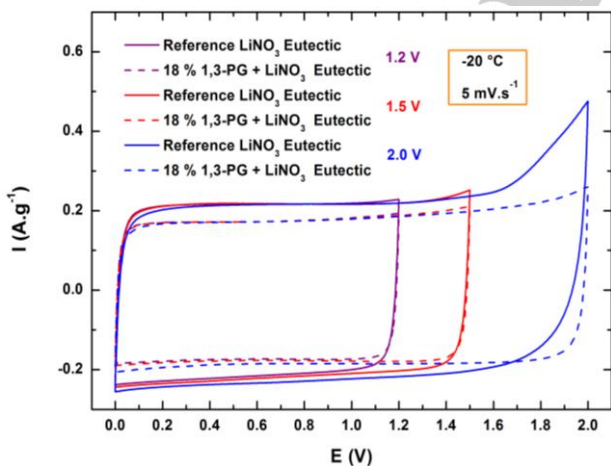
| Sample | This work | Aqueous electrolyte (mol·dm ⁻³) | | | Organic electrolyte (mol·dm ⁻³) | | |
|-----------------------------------|-----------|---|---|---------------------------|---|--------------------|--|
| | | K ₂ SO ₄ (0.5 M) | Li ₂ SO ₄ (2.0 M) | LiNO ₃ (5.0 M) | Et ₄ NBF ₄ PC (1.0 M) | ACN (1.0 M) | LiPF ₆ EC:EMC (3:7 vol.%) (1.0 M) |
| η (mPa·s) at 25 °C | 3.13 | 0.60 ⁶⁶ | 2.49 ⁶⁸ | 1.3 ⁶⁹ | 3.72 ⁷⁰ | 0.57 ⁷² | 2.7 ⁷³ |
| σ (mS·cm ⁻¹) at 25 °C | 67.5 | 81.0 ⁶⁷ | 83.6 ⁶⁸ | 165 ⁶⁹ | 12.6 ⁷¹ | 63.0 ⁷² | 9.3 ⁷³ |

Potential window

Cyclic voltammetry (CV) measurements were performed at 5 mV·s⁻¹ for different potential windows in order to determine the operating potential. As the minimum operating temperature for the eutectic used as reference is -20 °C,²⁰ the potential window investigation is firstly performed at this temperature (Fig. 5). As expected, a classic rectangular shape, representative of a typical EDLC reversible capacitive behaviour, is obtained. Until 1.6 V both electrolytes exhibit the same electrochemical stability while over 1.6 V only the ternary electrolyte maintains its stability (no electrochemical reaction), e.g. oxidation process started for the eutectic electrolyte. One can notice that, despite that the ionic conductivity was halved (40 mS·cm⁻¹ against 18 mS·cm⁻¹) by the addition of PG, 82 % of the capacitance is still conserved.

Coulombic efficiency and polarization

The optimal potential window is usually determined using the coulombic efficiency with an acceptable value of 97 %. However, this method is mostly based on the apparition of the oxidation wall/peak with the potential increase without the polarization phenomena. A strong polarization occurring through oxidation process can easily counter-balance the larger area (leading to a higher but erroneous value of capacitance) due to the oxidation peak apparition. Consequently, these two criteria have to be considered for identifying the more accurate operating voltage.

**Figure 5** CVs at 5 mV·s⁻¹ at -20 °C and different potential windows for the reference (LiNO₃ eutectic) and 18 % 1,3-PG + LiNO₃ eutectic.

Firstly, the polarization impact has to be quantified. Herein, we proposed a simple and accessible method. Whether in oxidation or reduction (Fig. 6), this calculation is based on the ratio between the considered section, from the experimental curve (---) and the extrapolated curve (—), based on the experimental data, without any polarization phenomena (ideal case), following next equations:

$$Pol_{Ox} = \frac{A_{Ox,exp}}{A_{Ox,ideal}} \times 100 \quad (3)$$

$$Pol_{Red} = \frac{A_{Red,exp}}{A_{Red,ideal}} \times 100 \quad (4)$$

With Pol, the gap to ideality, A_{exp} (▨) and A_{ideal} (■), experimental and ideal areas respectively in oxidation and reduction. The ideal area is calculated as follow:

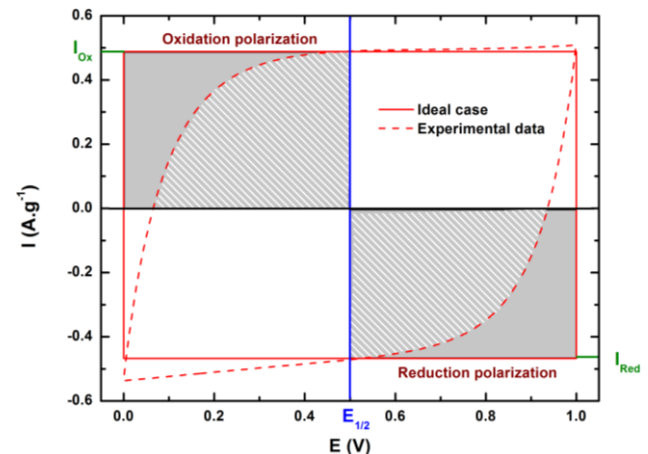
$$A_{ideal} = E_{1/2} \times I_{Ox} \text{ OR } I_{Red} \quad (5)$$

With $E_{1/2}$ the half of the operating voltage and I_{Ox} and I_{Red} the corresponding currents, respectively in oxidation and reduction. The last parameter defined is the polarization factor (PF) and is calculated based on equation E4:

$$PF = |Pol_{Ox} - Pol_{Red}| \quad (6)$$

As expected, the PF should be as close as possible to 0 and calculated for $Pol_{Ox/Red} > 95\%$ at least for 20 °C. Then this value should be adapted to the studied temperature as kinetic parameters are affected.

Finally, the optimal operating voltage is determined for the best combination of the coulombic efficiency (> 97 %) and a PF close to 0 with minimal value of $Pol_{Ox/Red}$ according to Table 5. In the Fig. 7, the novel ternary electrolyte was compared to the eutectic binary mixture of water and LiNO₃ depicted as the reference low temperature aqueous electrolyte in term of polarization and coulombic efficiency on a range of potential (0.8 to 2.4 V) at -20 °C. The reference electrolyte was exhibiting a slightly increase of polarization from 90 % to 95 % when the potential is set up from 0.8 to 1.6 V with PF values ≤ 5. Higher potentials lead to equal or reduced values of polarization accompanied with PF values superior to 10. At the same time coulombic efficiencies were quite stable until 1.6 V and were rapidly decreasing after 1.8 V.

**Figure 6** Theoretical approach for the evaluation of polarization.

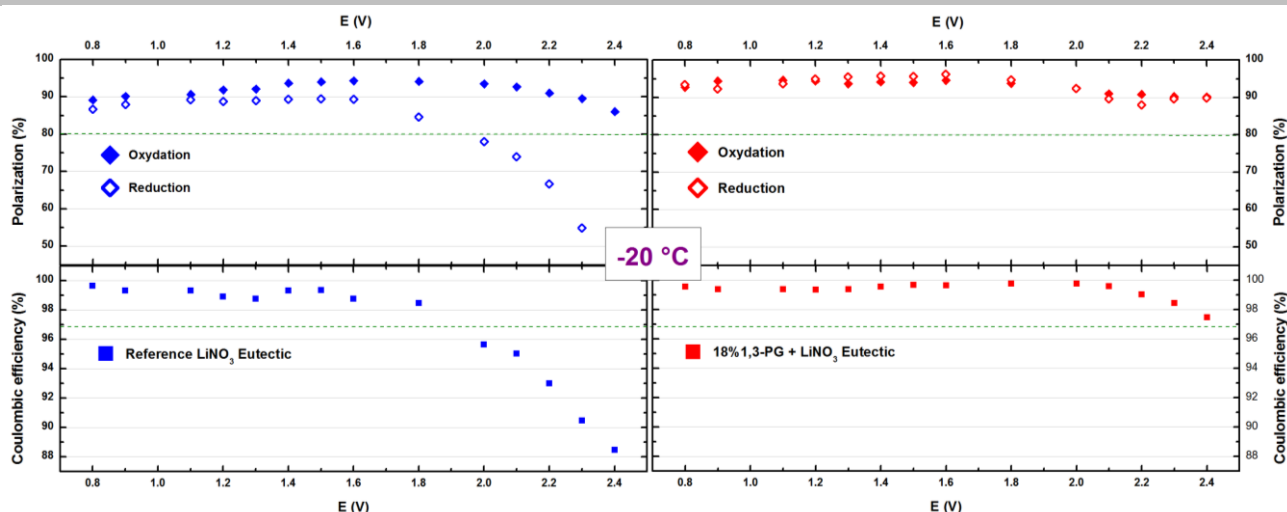


Figure 7 Polarization and coulombic efficiency at -20 °C as function of the operating voltage for the reference (LiNO₃ eutectic) and 18 % 1,3-PG + LiNO₃ eutectic.

Table 5 Theoretical value of parameters related to polarization phenomena.

| T (°C) | Pol _{Ox/Red} (%) | PF |
|--------|---------------------------|-----------|
| 20 | ≥ 95 | 0 ≤ x ≤ 5 |
| 0 | ≥ 90 | |
| -20 | ≥ 80 | |
| -40 | ≥ 70 | |

These data perfectly match, meaning that the maximal operating voltage at -20 °C for the LiNO₃-water eutectic mixture is 1.6 V. On the side of the ternary electrolyte, polarizations were stable and superior to 90 % on all the potential range with a maximum of 96% reached at 1.6 V. Moreover, PF values were almost not varying with an average around 2 and a maximum of 2.8 reached at 2.2 V. Coulombic efficiencies were following the same behaviour with a slight divergence starting at 2.0 V with a trend of decreasing efficiencies from 99.8 % to 97.5 % at 2.4 V. With all of this data, the upper limit of potential can be determined as being 2.0 V, thus showing that our ternary electrolyte presents, in addition to its performances at low temperature, an extended potential window. This parameter can be related to two factors, the first one is that the addition of a

significant amount of a compound from the alcohol family, whose majority of their oxidation potentials are greater than 2 V (vs. Li/Li⁺) makes it possible to enlarge the potential operating window of the composite electrolyte leading to greater energy density. The second one is the limitation of the free-water amount *via* a significant concentration of LiNO₃ (20.09 wt.%) and the impact of 1,3-PG on solvation, propylene glycol could solvate or be solvated by water.

Floating tests

In order to verify the stability of the devices, floating tests were carried out. Firstly, they were performed at the optimal potential for each electrolyte as previously determined (*i.e.* 1.6 V and 2 V), for a duration of 144 h at -20 °C in order to compare the ternary electrolyte to our reference (binary eutectic composition) as shown in Fig. 8. Fig. 9 (a) shows the electrochemistry Nyquist plots for the two electrolytes before and after floating. Both devices exhibit high stability as impedance diagrams are perfectly and nearly stackable respectively for the ternary and binary mixtures. Moreover, the supercapacitors show typical EDLC behaviour coupled to low ESR (< 5 Ω) and represented by Warburg semi-infinite diffusion and capacitive contributions at respectively medium and low frequencies. Due to larger solvated ions and slower mobility, the diffusion process is longer for the system based on the ternary electrolyte. The only significant difference appeared in the capacitive part of the 1,3-PG curve after 144 h of floating, a slightly higher resistance is responsible for a smaller angle of the diffusion slope.

In term of pure performance, both electrolytes conserve 84 % of their initial capacitances (respectively 36.9 F·g⁻¹ and 27.4 F·g⁻¹) after 144 h of floating. By comparing the charge transfer resistance of the selected electrolytes, *i.e.* binary (6 Ω) and ternary (18 Ω) mixtures (Fig. 9.a), one can highlight that the addition of the PG strongly affects the interface electrode/electrolyte layer caused by an increase of the solvation shell. Furthermore, floating tests at higher potential (2.2 V for 144 h) were performed at -40 °C on this system in agreement with the Fig. 8 which shows the optimal potential (efficiency and polarization) at 2.2 V. The resulting electrochemistry Nyquist plots are depicted in Fig. 9 (b). Once again, an excellent stability and a low electrolyte resistance (for

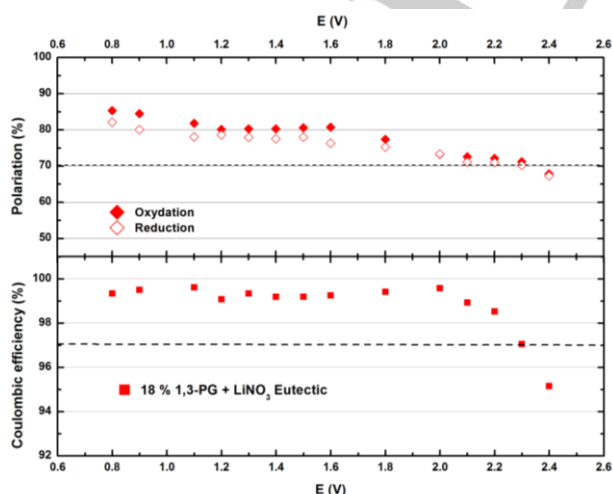


Figure 8 Polarization and coulombic efficiency at -40 °C as function of the operating voltage for the 18 % 1,3-PG + LiNO₃ eutectic.

such temperatures) are obtained. The system is perfectly stable after 108 h of floating (Fig. S2 in ESI) followed by a slightly

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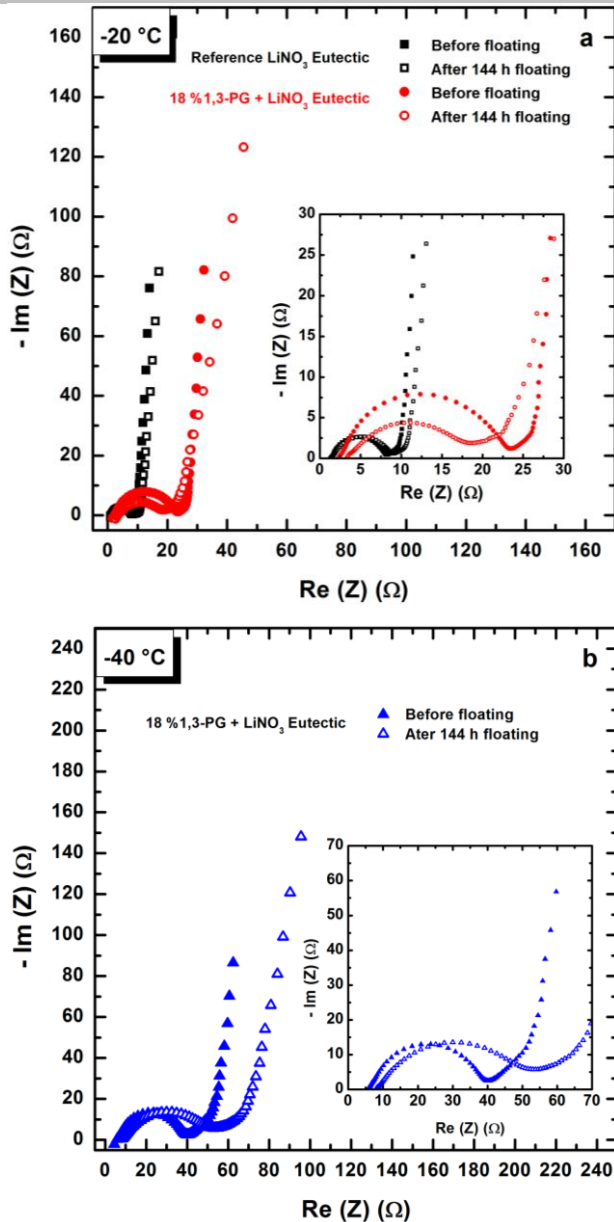
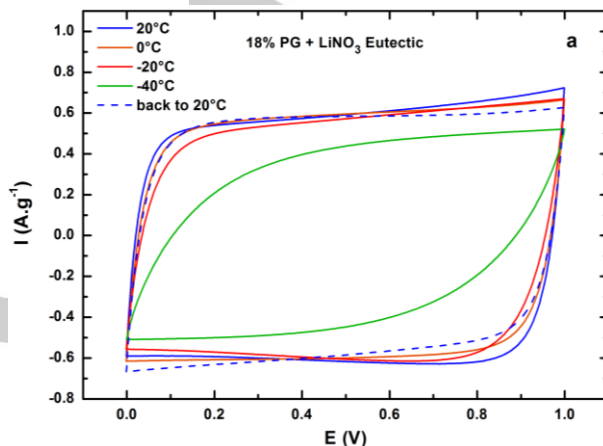


Figure 9 Electrochemistry Nyquist plots before and after 144 h of floating of (a) the reference (LiNO₃ eutectic) and 18 % PG + LiNO₃ eutectic at -20 °C and (b) 18 % 1,3-PG + LiNO₃ eutectic at -40 °C.



This evolution is accompanied by a decrease of the angle of the diffusion slope characteristic of slower diffusion kinetics through the carbon porosity. This stability is also represented by the conservation of 86 % and 73 % of the initial capacitance (24.1 F·g⁻¹) respectively after 108 h and 144 h of floating.

Temperature resilience

The capabilities of our electrolyte to overcome large temperatures up and down were investigated by performing CVs at higher and lower temperatures and then return back to the initial one. This test was carried out from 20 °C to -40 °C, on a potential window of 1 V, thus, the obtained curves are plotted together in Fig. 10 a, and resulting capacitance retentions as function of the temperature in Fig. 10 (b). From 20 °C to -20 °C, CVs were pretty close, and only few polarizations could be highlighted. However, at -40 °C, currents are lower and the polarizations both in oxidation and reduction are much more pronounced because of less advantageous diffusion kinetics. Nevertheless, the return to 20 °C allows a return of currents and curves similar to the initial state underlining the resilience of our electrolyte toward large temperature variations. On the capacitance side (Fig. 10 (b)), a loss of less than 6% with a drop of 40 °C between 20 and -20 °C is observed (from 29.1 to 27.4 F·g⁻¹). The difference is greater at -40 °C with a loss of 29% of initial performances, but the capacitance remains highly decent for these temperatures (20.6 F·g⁻¹); finally, when returning to 20 °C, the initial capacitance is fully recovered, indicating that, no matter if our ternary mixture does not correspond to an invariant composition (phase diagram), due to a very low liquidus.

Performances comparison

In order to evaluate the EDLC device performances (operating temperature and voltage, power and energy densities), they were determined at 1 A·g⁻¹ based on the following equations:

$$E = \frac{1}{2} C V^2 \tag{7}$$

With E the energy density, C the gravimetric capacitance and V the operating voltage.

$$P = \frac{E}{t_{\text{discharge}}} \tag{8}$$

With P the power density, E the energy density and t_{discharge} the

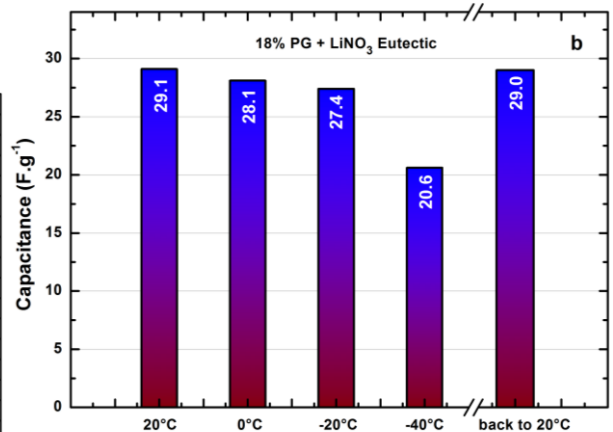


Figure 10 (a) CVs at 5 mV·s⁻¹ of the system AC//AC with electrolyte 18 % 1,3-PG + LiNO₃ eutectic and (b) the capacitance retention regarding the operating temperature.

increase of the charge transfer resistance (from 37 Ω to 45 Ω).

discharge time.

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Table 6 Evaluation and comparison of performances, toxicity and cost.

| System | Op.Temp. (°C) | ΔV (V) | I (A·g ⁻¹) | E (Wh·kg ⁻¹) | P (Wh·kg ⁻¹) | Evaluation | Ref. |
|---|---------------|----------------|-------------------------|-----------------------------|--------------------------|------------|-----------|
| 1,3-PG:H ₂ O + LiNO ₃ (3.65 m) | -40 | 2 | 1 | 13.1 | 2040 | | This work |
| ACN:Dioxalane + Et ₄ NBF ₄ (0.75 mol·dm ⁻³) | -70 | 2.5 | 1 | 10.8 | 2580 | | [8] |
| ACN:H ₂ O + LiTFSI (5 m) | -30 | 2.2 | 1 | 14.8 | 5320 | | [23] |
| ACN:H ₂ O + NaClO ₄ (17 m) | -50 | 2.3 | 0.5 | 20.1 | 560 | | [24] |
| DMSO:H ₂ O + LiTFSI (6.6 m) | -35 | 2.5 | 1 | 22 | 350 | | [25] |
| MeOH:H ₂ O + Li ₂ SO ₄ (0.7 mol·dm ⁻³) | -40 | 1.6 | (2 mV·s ⁻¹) | (C = 19 F·g ⁻¹) | | | [26] |



These performances, as well as the toxicity and the cost, were compared to similar studies, using commercial activated carbon and comparable current density. As other parameter (Fig. S3 of the ESI), the time constant is determined using the Bode phase plots to evaluate the charging time of the different related devices.

In term of pure electrochemical performances, the device using LiTFSI in ACN:water mixture demonstrates higher power densities (5320 Wh·kg⁻¹). However, on the down side, this electrolyte is toxic and expensive mainly due to the use of LiTFSI as salt in a significant concentration. Furthermore, the system using dioxalane mixed with ACN is economically interesting, but it remains the more toxic. In spite of intermediate power and energy densities, our system appears as the best bargain as it is the cheaper one (0.24 \$·g⁻¹ as shown in Tables S2 and S3 in ESI) and the less toxic with electrochemical performances close to or higher than the other hybrid electrolytes.

Conclusion

In summary, we designed a strategy to develop a greener electrolyte for low temperature applications. It is based on the non-toxic and cost-efficient eutectic system LiNO₃ in water and its improvement. A specific evaluation of toxicity and safety of several organic solvents was performed leading to the selection of propylene glycol isomers as co-solvents. Based on pure physico-chemical property (viscosity), 1,3-propylene glycol (1,3-PG) was selected for designing a ternary electrolyte enabling low-temperature supercapacitor applications. Several compositions were investigated by DSC and the 18 % 1,3-PG + LiNO₃ eutectic exhibits a wide liquid range (< -40 °C to 60 °C).

Due to relatively high concentration, this electrolyte has transport properties comparable to classic aqueous electrolytes and higher than common organic electrolytes. A specific

calculation, based on usual redox phenomena but coupled to polarization effect, was set up in order to evaluate efficiently the optimal operating potential window. According to this method, the optimal operating voltage is 2.0 V at -40 °C, although it can reach easily 2.4 V for smooth applications. Floating tests, performed at -40 °C and 2.0 V, highlighted the excellent stability over more than 100 hours of floating. Moreover, the capacitance showed a perfect temperature resilience as the device recovered nearly 100 % of initial capacitance (29 F·g⁻¹) after being set up back at 20 °C from -40 °C. Compared to other devices, our system exhibits intermediate energy (13.1 Wh·kg⁻¹) and mildly high power (2040 W·kg⁻¹) densities nevertheless registering in the current environmental and safety policies in contrary to compared devices. This unique work opens doors for the design of synergistic electrolytes in term of performances, eco-toxicity and cost (as evaluated in Table S3 of the ESI) in direct line with contemporary research efforts.

Experimental Section

All reagents, procedures and subsequent data are available in the Supporting Information.

Acknowledgements

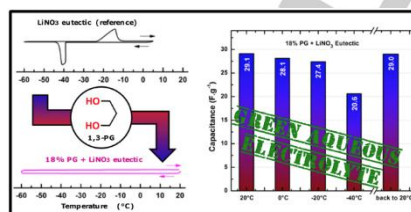
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Keywords: water-based eutectic system • electrostatic double-layer capacitor • toxicity • eco-compatibility • cost

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Entry for the Table of Contents



Electrochemical energy storage devices require a global and synergetic approach to design safer-by-design and sustainable electrolytes. An unprecedented strategy was then performed taking into account their toxicity, eco-compatibility and cost while targeting low temperature applications by obtaining a ternary electrolyte based on a eutectic system LiNO₃ in water.