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Perspective—Semi-Solid Electrolytes Based on Deep Eutectic Solvents: Opportunities and Future Directions

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In the past years the interest in deep eutectic solvents (DESs) has been steadily increasing, much due to the possibilities to rationally design their special physical properties by choosing the right combination of components. This perspective aims to help unifying how deep eutectic solvents should be reported and explores the vast opportunities for semi-solid electrolytes based on DESs. The latter connects well to the trend on research towards solid-state energy storage devices, emphasizing the aim of increased safety.

The choice of a suitable electrolyte for electrochemical energy storage devices, e.g. batteries, supercapacitors and their hybrids, remains one of the most challenging problems. This as liquid electrolytes, the paradigm today, suffer from poor intrinsic security (e.g. electrolyte leakage, thermal runaway) and contributes to limited cell power density (as safety systems are needed),[1,2] while solid-state electrolytes (SSE) have poor solid-solid contact between electrolyte-electrode interfaces and particles in electrodes resulting in large interfacial resistances.[1,3] A semi-solid electrolyte (SeSE, also known as a quasi-solid-state electrolyte), i.e. a liquid electrolyte immobilized in a solid matrix, may offer the synergies and even novel properties bringing new options for electrochemical devices. The use of SeSE in supercapacitors,[4–9] metal ion capacitors,[10–13] and batteries[14–19] have endowed them with mechanical robustness and excellent transport efficiency of ion or solute.

Deep eutectic solvents (DESs) are systems formed from a mixture of two solid organic materials that yields a free-flowing solution with a melting temperature below that of an ideal liquid mixture.[20,21] DESs is a rapidly developing area of research, especially when targeting electrolytes for electrochemical devices, as some of their tailored features include low precursor cost—especially as compared to ionic liquids, high ionic conductivity, high solvation ability, large mutual solubility with metal salts, wide electrochemical stability windows, and absence of secondary reactions such as water electrolysis, especially as compared with traditional organic solvents.[22–27] Combining the two by encapsulating a DES in a SeSE, i.e. a SeSE_DES, aims primarily to improve the safety of batteries and supercapacitors as compared to liquid electrolytes, which in general, have risks of leakage and flammability.

Current Status

The first DES was obtained by Abbott et al.[28] in 2003 by mixing a hydrogen bond acceptor, choline chloride, with a hydrogen-bond donor, urea, where the charge delocalization occurring through hydrogen bonding between the halide ion and the hydrogen-donor moiety is responsible for the lowered melting point.[29,30] Although Abott et al.[28] first defined DESs as hydrogen bond complexes with an eutectic point, i.e. the composition of lowest freezing point and viscosity, introduction of new complexes have led to an over-generalization of the definition resulting in several misconceptions. Recently, Martins et al.[20] and Kollau et al.[21] defined DES as "a mixture of pure compounds (e.g. C_1 and C_2) for which the eutectic

point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from ideality. The temperature depression (Fig. 1a) should be defined as the difference (ΔT) between the simple ($T_{E,simple}$) and the deep ($T_{E,deep}$) eutectic point. Additionally, the temperature depression should be such that the mixture is liquid for a certain composition range (any mixture between x_1 and x_2 in Fig. 1a)." This stricter definition allows for a better differentiation between eutectic mixtures as either "simple" or "deep." Moreover, this requires authors to make solid-liquid equilibria (SLE) phase diagrams and the melting properties of the pure compounds available. The various interactions present in the mixture, i.e. C_1-C_1, C_2-C_2, and C_1-C_2, are responsible for the ideality or non-ideality of the liquid phase. If all the components in the mixture follows the ideal solubility curve this means that the interactions between the components are not significantly different from those present in the pure compounds. DESs should thus present significant negative deviations from this ideality ($\Delta T > 0$). However, in cases where the difference is small, a deeper analysis of the SLE phase diagram can be helpful as it might be the case that only one of the solubility curves deviates from ideality (Fig. 1b).

Similarly to ionic liquids, DESs have been used in various fields of electrochemistry as electrolytes or solvents.[31–49] Most of the reports of DESs in batteries[27,50–55] and supercapacitors[27,56–60] have shown that they have properties desirable for these applications (e.g. excellent thermal stability, broad electrochemical stability and low viscosity); however, it must be noted that their ion conductivity is still inadequate for some applications.[50]

A comprehensive study focusing on the ion conductivity of three commercial DESs; ethaline, glyceline and reline, was recently published,[61] and in order to further increase the conductivity of these DESs, the authors suggest three strategies: lowering the glass transition temperature, increasing the fragility of the system,[62,63] and/or reducing the translational–rotational coupling. It has already been shown that confining ILs in gels, i.e ionogels, leads to a destructuration of the IL due to the interfacial effect and this reduces the fragility. This results, locally at the interfacial region, in short relaxation times, low viscosity, and good ion conductivity.[64] Although ILs have been immobilized in organic (e.g. polymer), inorganic (e.g. silica or carbon nanotube) and hybrid (e.g. silica and dicarboxylic acid) solid networks[65] for electrochemical applications, DESs have received less attention.

A SeSE_DES is also a promising approach to improve the safety of any electrochemical energy storage device, including batteries and supercapacitors, as these materials are highly stable over time and would keep the specific properties of DESs except flowability. Compared to liquid electrolytes, the SeSEs show much higher
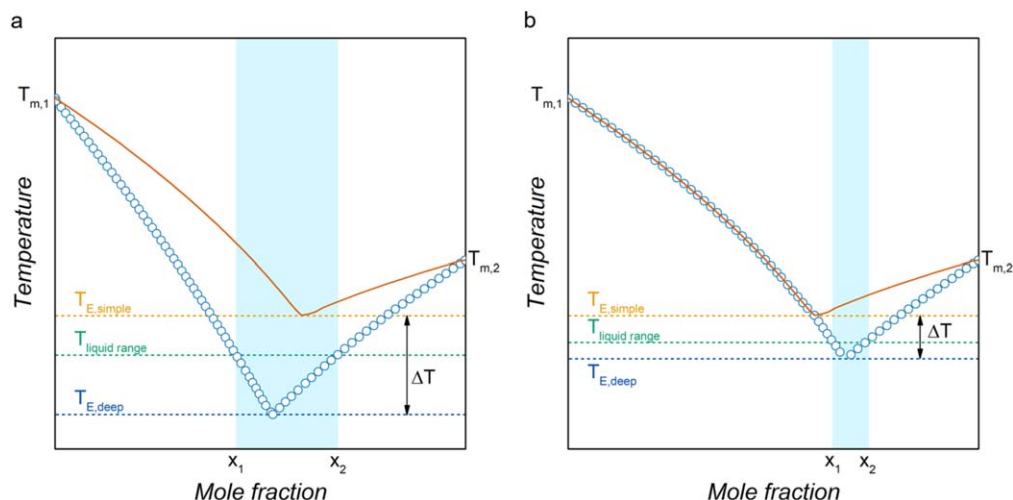
zE-mail: adriana.navarrosuarez@chalmers.se

Figure 1. Schematic representation of the comparison of the SLE phase diagram of a simple eutectic mixture (orange line) and a deep eutectic mixture (blue circles). (a) Interactions C_1-C_2 are stronger than C_1-C_1 and C_2-C_2. (b) Interactions C_1-C_2 are stronger than C_2-C_2 but weaker than C_1-C_1. Adapted from Martins et al.[20]

thermal stabilities, which opens for devices with both higher and wider operating temperature windows.[66–68] Moreover, for batteries using metal anodes the SeSEs is a very promising concept to prevent the detrimental dendrite formation and hence cell failure.[66,69–72]

Most of the SeSE_DES reported to date are based on the original choline chloride:urea mixture or slight variations. In one of the first studies, Ramesh et al.[73] used DESs formed by choline chloride and urea as supramolecular gelators (also known as low molecular mass gelators or molecular gels) to plasticize corn starch (CS) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to create polymer electrolytes. The maximum ion conductivity, ∼1 mS · cm^{-1} at room temperature, was obtained for a sample with a composition CS: LiTFSI:DES 14:6:80. However, this approach does not really take advantage of the DES properties as electrolyte/solvent, but rather as a gelator.

To the best of our knowledge, the first SeSE that benefited from the properties of DES as electrolyte was developed by Mukesh et al.[74] who polymerized 2-hydroxyethyl methacrylate in the presence of choline chloride (HBA) and orcinol (HBD), resulting in the formation of a highly stretchable gel (>30 times) that demonstrated good capacitive behaviour with metal oxide frameworks (>200 F · g^{-1}). More recently, Ruiz-Olles et al.[75] took advantage of the solvation abilities of DES by using choline chloride with different alcohols and ureas and 1,3:2,4-dibenzylidene-D-sorbitol as a gelator. These gels tolerated the presence of ionic additives such as lithium, magnesium and calcium ions; hence, they suggested the use of these electrolytes in Li-ion batteries since they achieved moderate ion conductivities, 3–4 mS · cm^{-1}, at room temperature.

Panzer's group has been working on developing DES gel electrolytes, and so far they have immobilized choline chloride and ethylene glycol in either poly(2-hydroxyethyl metacrylate)[76] or in gelatin from porcine skin.[77] The former was tested as electrolyte in a supercapacitor prototype with activated carbon fabric electrodes achieving 33.3 F · g^{-1} at 0.01 A · g^{-1} while the latter was used for ionic skin applications.

The problem with DESs formed by choline chloride is that the decomposition of pure choline chloride near the melting point precludes the direct measurement of its melting properties, making it impossible to thermodynamically characterize the choline-based eutectic systems and their SLE phase diagrams.[78] Here computational approaches could help in the development of models to describe the phase behaviour of both reported DESs and for the design of new ones.

The misconception of the DES definition has resulted in several studies describing SeSE_DES without proving the deep eutectic properties of the solvent, but rather just defining them by their hydrogen bonding or physical state at room temperature. Rahman et al.[79] electrospun a poly(vinyl alcohol) membrane that was soaked in a series of solvents based on N,N-diethylethanolammonium chloride and ethylene glycol reaching electrical conductivities of up to 22.7 mS · cm^{-1}. Although this approach could be used to encapsulate DESs, the authors failed to prove any deep eutectic properties of their solvent as the only parameter used to choose the ratio between the components was the conductivity and not the melting points. Luo et al.[80] reported a solid polymer electrolyte by cross-linking 1-methyl-2-pyrrolidone, polyvinylidene fluoride, and a "DES" prepared from choline chloride and 1,3-butanediol, but no SLE phase diagram was reported.

Generally, the addition of a salt to a solvent increases the viscosity as much stronger ion–ion interactions are introduced, rendering slower dynamics and transport properties.[81] Therefore, creating an SeSE where the liquid component exclusively depends on the DES, i.e. having the charge carrier as part of the DES structure, is of special interest to electrochemical applications. Joos et al.[82] immobilised a DES composed of LiTFSI and methylacetamide (MAc) within a silica matrix and also coined it an "eutectogel." The resulting electrolyte achieved ion conductivities of ∼1.5 mS · cm^{-1} at 25 °C and when it was employed in a Li/lithium iron phosphate cell set-up delivered 105 mAh · g^{-1} at a 0.1 C-rate. Their DES was based on the DES first developed by Hu et al.[51] and Boisset et al.[27,53] Although they defined LiTFSI:MAc (1:4) as a DES based on the physical state of the mixtures at room temperature and showed the SLE phase diagram, they failed to show if there is any deviation from the ideal solubility curve. Figure 2 shows the SLE phase diagram involving LiTFSI and MAc,[53] and our calculated ideal solubility curves using:

$$\ln(x_i \gamma_i) = \frac{\Delta_m H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{\Delta_m C_p}{R}\left(\frac{T_m}{T} - \ln\frac{T_m}{T} - 1\right) \quad [1]$$

where γ_i is the activity coefficient of compound i (set to 1 here) at a certain liquid mole fraction composition x_i, T is the absolute temperature, T_m and $\Delta_m H$ are the melting temperature and enthalpy of the pure compound, respectively (i.e. T_m and $\Delta_m H$ for LiTFSI[83] is 509.15 K and 13.2 kJ · mol^{-1}, respectively, and for MAc[84] 303.8 K and 10.1 kJ · mol^{-1}), R is the universal gas constant, and $\Delta_m C_p$ is the difference between the molar heat capacity of compound i in the liquid and solid phases. Experimental data of $\Delta_m C_p$ was not available, but some authors[85] reported it to be between 0 and the entropy of fusion at the melting point ($\Delta S_m = \Delta_m H / T_m$). Hence, we here present possible representations for the ideal solubility curves based on $0 \leqslant \Delta_m C_p \leqslant \Delta S_m$.
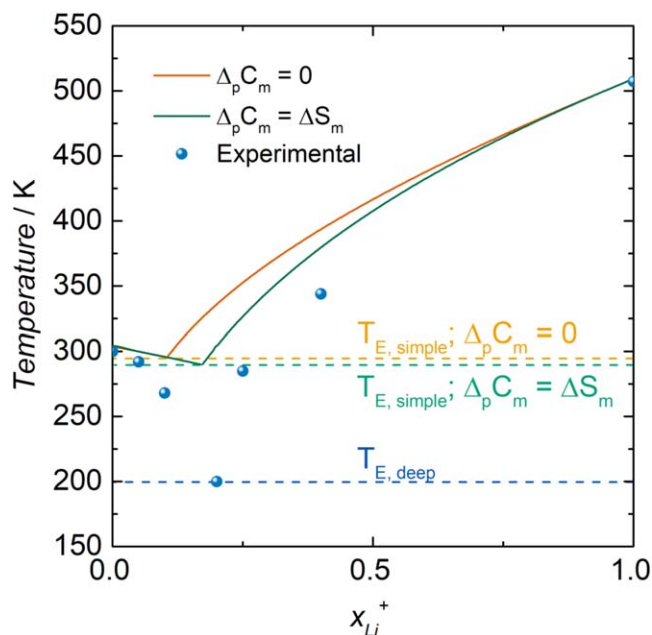
Figure 2. SLE phase diagram of mixtures composed of LiTFSI and MAc. Blue circles represent experimental data[53] while lines represent the ideal solubility curves at different molar heat capacities.

The SLE phase diagram of LiTFSI:MAc shows a negative deviation from ideality for both components suggesting that the LiTFSI-MAc interactions are significantly stronger than both those of LiTFSI-LiTFSI and MAc-MAc, proving the mixture to be a DES, and making these "eutectogels," to the best of our knowledge, the first SeSE_DES not based on choline chloride and a viable option for Li-ion batteries.

Future Needs and Prospects

DESs have been described as green, environmentally friendly, and non-toxic[23]; however, these characteristics depend both on the individual components and their mixture(s). Hayyan et al.[86] studied the cytotoxicity of choline chloride based DESs with four hydrogen bond donors (e.g. glycerine, ethylene glycol, triethylene glycol and urea). Even though there was no toxicity effect on the studied bacteria, the cytotoxicity of the DESs was much higher than that of the individual components.

Choosing a DES with a wide liquidus temperature range will be beneficial for electrochemical devices as this would avoid undesirable salt precipitation to occur during cycling. This is especially important for systems such as LiTFSI:MAc where the charge carrier is part of the DES structure and the oxidation state of the components would change upon cycling. *Operando* studies would be necessary to unravel the occurrence and impact of any electrolyte phase changing mechanisms.

MAc based DESs, with LiTFSI, lithium nitrate, or lithium hexafluorophosphate as the salt, have been tested as electrolytes for lithium-ion batteries and using other metal salts e.g. sodium, calcium based on the same anions, might lead to the development of electrolytes for next-generation batteries—much needed.[87,88] A step in this direction has been recently been published by Qiu et al.[89] reporting a rechargeable zinc-ion battery based on an acetamide-Zn(TFSI)$_2$ eutectic electrolyte that outperforms other DESs formed by other common Zn salts (e.g., Zn(ClO$_4$)$_2$, Zn(CH$_3$COO)$_2$, and Zn(BF$_4$)$_2$). The cyclic stability of zinc/vanadium pentoxide (V$_2$O$_5$) cells using their electrolyte outperforms their aqueous counterparts for each current density. At 200 mA g^{-1} the former delivers an excellent stability with a high capacity retention of 91.3% with a high coulombic efficiency ∼99.34% for 100 cycles.

The term "eutectogel" should be treated carefully as it does not emphasize the "deep" property of the solvent, nevertheless, this family could be extended to other gel-like materials as they can be prepared through sol-gel, solvent casting, swelling of the matrix in DES, hot pressing, or in situ polymerization. Moreover, by developing a single-step preparation with the electrode there is the opportunity to better integrate the electrolyte into non-traditional geometries, as solidification occurs after complete wetting of the structure.[90]

Nevertheless, research should not be constricted to gels, as designing both the DES and the host support will allow the synthesis of a SeSE_DES for specific uses. For example, in the area of structural energy storage devices, which combines structural performance with energy storage, robust SeSE_DES are of particular interest as they would provide a solid-state matrix with conductivities similar to liquid electrolytes.[91,92]

Several reports on polymerized DESs (DESs that contain polymerizable units and are conductive after polymerization) have been published lately,[93–102] and although there could be potential applications for these materials, most authors have failed to prove that the initial mixtures are in fact DESs. Moreover, the only advantages reported for these polymerized DES are easy preparation, 100% atom utilization and low cost as DESs[93]; implying that there is no need for the monomers to initially form a DES. Further studies are needed to verify the advantages of starting with a DES and to fully understand the system after polymerization.

SeSE_DES might also be applied in "dual-ion" batteries or "dual-carbon" batteries, novel energy storage devices in which the electrolyte serves as active material besides carrying charge between the anode and the cathode. As major goal for this system is to find suitable electrolyte mixtures which exhibit not only a high oxidative stability at the cathode, but also form a stable solid electrolyte interphase at the anode.[103]

By combining specific surface designs with the DES properties, a vast number of materials with properties that might improve current devices or help in the development of new technologies can be developed. A full understanding of the interactions between the components of the SeSE_DES is of utmost importance to maximize the advantages of these electrolytes.

Concluding Remarks

SeSE_DES represent a promising development emerged from the interface of semi-solid electrolytes and deep eutectic solvents. However, there are still many challenges that must be addressed for these nanocomposites to reach their full potential. A must for these systems is to provide the SLE phase diagram of the liquid electrolyte and its melting properties to confirm the deep eutectic nature of the solvent. Further property improvements will be obtained by developing specific surface designs that achieve efficient solid-solid electrode-electrolyte interfaces without any side reactions.

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