Solvent-free lithium and sodium containing electrolytes based on pseudo-delocalized anions†

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Mixing the standard battery salt LiTFSI with various Li-salts of novel pseudo-delocalized organic anions \(\text{[N(CH}_2\text{)}_2\text{((CH}_3\text{)}_3\text{SO}_2\text{)](CH}_3\text{)}_2\text{SO}_3}^-\) (MM\(_{\text{mix}}^-\)), results in super-cooled solvent-free liquid electrolytes with glass transition temperatures of ca. 50°C. Synthesis routes and full chemical characterisation of the new pseudo-delocalized anions are presented, as well as phase and thermal stabilities. The ion conductivities and electrochemical stabilities are evaluated towards lithium and sodium battery application.

Conventional lithium-ion battery (LIB) electrolytes are composed of lithium salts with weakly coordinating anions, such as hexafluorophosphate\(^{1}\) (PF\(_6^−\)), tetrafluoroborate\(^{2}\) (BF\(_4^−\)), bis(oxalate)borate\(^{3}\) (BOB), or bis(trifluoromethanesulfonyl)imide\(^{4}\) (TFSI), dissolved in a mixture of organic solvents (often linear and cyclic carbonates) at ca. 1 M concentrations.\(^{5,6}\) Their wide electrochemical stability windows (ESWs) allow the use of high voltage positive electrodes, such as LiCoO\(_2\) (4 V vs. Li\(^+/\text{Li}\)) and graphite negative electrodes (0.1 V vs. Li\(^+/\text{Li}\)), by virtue of the creation of a solid electrolyte interphase (SEI). This, together with the large capacities of the electrodes, enable a very high specific energy. But the safety of LIBs remains a major concern mainly due to the highly flammable organic solvents used.

The combination of ever higher energy densities and voltages of the cells with the highly flammable organic solvents\(^7\) directs particular attention towards creating novel electrolytes with improved safety characteristics. For example, replacing the organic solvents by an ionic liquid matrix improves the thermal stability drastically and decreases the flammability,\(^8\) but at the same time, both the lithium transference number and the electrolyte fluidity often decreases, thus reducing the electrochemical performance.

All solid-state batteries (ASSBs),\(^9,10\) in which the conventional electrolytes have been replaced by a solid-state electrolyte (SSE), also claim to provide remarkable safety characteristics. However, most SSEs suffer from low room temperature ionic conductivities, often three orders of magnitude lower than liquid electrolytes, hence they usually operate at elevated temperatures (ca. 80°C),\(^11\) even if there exist polymer electrolytes with acceptable ionic conductivities at room temperature (1 mS cm\(^{-1}\)). As a result, however, the concept of high-temperature lithium-ion batteries (HT-LIB) has emerged.\(^12\)

Another alternative is “thermal” batteries, operating between 350°C and 550°C and employing molten salt mixtures as liquid solvent-free electrolytes, with high thermal stability, low flammability, and high ionic conductivity.\(^11\) In order to utilize this concept for LIBs, the melting temperature must decrease significantly – but even if these electrolytes do not reach the conductivities needed at room temperature, they might be applied in HT-LIBs. This has been achieved by combining two or three alkali cation salts with a common weakly coordinating anion, such as TFSI,\(^13,14\) bis(trifluoromethanesulfonyl)imide (FSI),\(^15\) or triflate.\(^16\) Such eutectic mixtures have promising ionic conductivities and form stable SEIs on typical LIB electrode materials. The molar fraction of Li\(^+\) is, however, quite low, which severely limits the rate capability of the cells despite the elevated operating temperature.\(^17\) Additionally, the presence of other alkali metal cations may interfere with the electrochemistry by unwanted plating or co-intercalation. The approach has its origin in enhanced ion conductivities by the “mixed alkali effect” of glassy and polymeric electrolytes, explored for batteries in the early 1990’s.\(^18,19\)

Herein, an alternative strategy is explored to create solvent-free electrolytes; mono-cationic–di-anionic mixtures, i.e. mixing two Li-salts with different anions, using the unique design of three different pseudo-delocalized (i.e. the negative charge...
delocalized by being localized at several central in the structure) anions \([\text{N(\text{CH}_3)\text{2}((\text{CH}_2)\text{3}\text{SO}_3)][(\text{CH}_2)\text{m}\text{SO}_3]}\) \((\text{MM}_{n=11}, \text{Fig. 1})^{20,21}\) – aiming primarily at HT-LIB application. We explore the previously reported lithium and sodium salts of MM\(_{4411}\) together with a new symmetric anion \((\text{MM}_{3311})\) as well as an asymmetric anion \((\text{MM}_{3411})\), all synthesized with high purity and excellent yield in three consecutive steps from readily available pre-cursors with minimal usage of solvent on multiple gram scale, expected to be scaled-up to kg scale without any practical difficulties. An electrolyte based 100% on salts is likely to initially be more expensive than a 1 M Li-salt liquid electrolyte, but improved battery safety and life-length may result. The here presented anions are likely to be cheap to produce based on the pre-cursors. The synthesis details and the full characterisation is found in the ESI.†

First, the thermal stabilities of the MM\(_{n=11}\) salts were assessed, wheathere their mixtures with TFSI salts were explored by constructing a series of quasi-phase diagrams highlighting the glass transition temperatures \((T_g)\) and melting points. Second, the ion conductivities as a function of both temperature and composition were studied and analysed using free volume theory. Finally, the lithium-only composition with the lowest \(T_g\) was selected for proof-of-concept electrochemical stability tests aiming towards lithium battery application.

The pure salts LiMM\(_{3311}\) and LiMM\(_{4411}\) exhibit very similar thermal behaviour. The first weight loss of \(~1.8\%\) at 140 °C is most likely due to residual water from the synthesis (Fig. 2a) as confirmed by TGA-FTIR evolved gas analysis (Fig. 2b), where the mass loss clearly observed in the derivates of the thermo-gravimetric signal (dTG) corresponds to an increased H\(_2\)O bend

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**Fig. 1** Chemical structures of the anions employed: (a) MM\(_{3311}\): 3.3’-[dimethylammonio]bis(propane-1-sulfonate), (b) MM\(_{3411}\): 4-[dimethylsulfonyl]ammonio]butane-1-sulfonate, (c) MM\(_{4411}\): 4.4’-[dimethylammonio]bis(butane-1-sulfonate), and (d) TFSI: bis(trifluoromethylsulfonyl)imide.

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**Fig. 2** (a) TGA traces of the LiMM\(_{n=11}\) salts (the corresponding NaMM\(_{n=11}\) salts present similar behaviour (Fig. S11, ESI†)), (b) FTIR band intensities evolution with temperature for the thermal analysis of LiMM\(_{3411}\) and (c) first derivative of the TGA signal of LiMM\(_{3411}\).

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**Fig. 3** DSC traces of the LiTFSI–LiMM\(_{3411}\) systems with compositions in molar fractions.
less coordinating Na⁺ cation. From DSC data, three quasi-phase diagrams were created for TFSI contents above 50 mol% (Fig. 4). These mixed anion-mixed cation systems have composition areas where no crystalline phases were observed. In the fully amorphous regions (blue), the partial substitution of Li by Na decreased the glass transition temperatures slightly (e.g. A to B in Fig. 4c). This effect was limited up to 20–30 mol% of Na⁺, where it favours the formation of crystalline phases above these concentrations. The trend observed for the binary systems extends to any cation composition and increasing the MMₓ₃₄₁₁ content (e.g. A to C in Fig. 4c) produces a corresponding increase in Tₛ. The ionic conductivities of Li[TFSI]₀.₈(MM₃₄₁₁)₀.₂, Li₀.₈Na₀.₂(TFSI)₀.₈(MM₃₄₁₁)₀.₂ and Li[TFSI]₀.₇(MM₃₄₁₁)₀.₃ all follow the same trend; cation substitution (Li to Na) produces only a two-fold increase, while anion substitution a two order of magnitude increase (Fig. 5a) – the latter is related to the glass transition temperatures (e.g. A to B in Fig. 4c).

The ionic conductivities of Li[TFSI]₀.₈(MM₃₄₁₁)₀.₂, Li₀.₈Na₀.₂(TFSI)₀.₈(MM₃₄₁₁)₀.₂ and Li[TFSI]₀.₇(MM₃₄₁₁)₀.₃ all follow the same trend; cation substitution (Li to Na) produces only a two-fold increase, while anion substitution a two order of magnitude increase (Fig. 5a) – the latter is related to the glass transition temperatures (e.g. A to B in Fig. 4c).

The effect is less evident at higher temperatures as the free volume in the structure decreases. The free volume in the structure decreases with increasing temperature, which leads to an increase in the ionic conductivity. The Arrhenius plots of the ionic conductivities of (a) Li[TFSI]₀.₈(MM₃₄₁₁)₀.₂, Li₀.₈Na₀.₂(TFSI)₀.₈(MM₃₄₁₁)₀.₂ and Li[TFSI]₀.₇(MM₃₄₁₁)₀.₃ and (b) for mixtures with different MMₓ₃₄₁₁ anions.

**Fig. 5**  Arrhenius plot of the ionic conductivities of (a) Li[TFSI]₀.₈(MM₃₄₁₁)₀.₂, Li₀.₈Na₀.₂(TFSI)₀.₈(MM₃₄₁₁)₀.₂ and Li[TFSI]₀.₇(MM₃₄₁₁)₀.₃ and (b) for mixtures with different MMₓ₃₄₁₁ anions.

**Fig. 6** Schematic of possible aggregate structures.

Flow. The Vogel temperature (Tᵥ) is related to the point where the glass transition temperature (Tₛ) is related to the free volume in the structure disappears. For the mixtures based on MM₃₄₁₁, slightly lower Tᵥ are obtained than for the MM₃₃₁₁ and MM₄₄₁₁ based mixtures (Table S2, ESI†). This might be related to the difficulty of forming organized structures by asymmetric anions, providing lower viscosity and higher conductivity (Fig. 5b). The way the different ions interact and organize themselves at temperatures above Tᵥ affects their mobility, which is roughly inversely proportional to their ionic radii. Hence, the large MMₓ₃₄₁₁ and TFSI anions are very unlikely to find accessible free volume of suitable size in their local environment, rendering them largely immobile. The lithium cation transference number is therefore expected to approach unity, but the total ion conductivities are still 1–2 orders of magnitude lower than other types of single-ion conductors, such as some block copolymers or crystalline LISICON-type electrolytes. The main difference from our single-ion conductor systems is the fact that they are liquids at moderate temperatures (ca. 60 °C) and therefore they are difficult to compare directly.

Kubota and Matsumoto reported on a more closely related system, with a bulky anion similar to TFSI operating at 150 °C, resulting in a very high Li⁺ transference number of 0.94. Compared to the system of Kubota (10⁻² S cm⁻¹ at 100 °C), the rather low conductivities observed here are likely due to the higher viscosities from our larger anions and a higher degree of ion association. Speculatively the sulfonate groups of the MMₓ₃₄₁₁ anions might act as Li⁺ traps and promote the formation of large aggregates (Fig. 6). The local structure was unfortunately not possible to be unambiguously resolved by e.g. IR or Raman spectroscopy (not shown). The partial substitution of Li⁺ by Na⁺ perturbs the aggregate structure, creates free volume, and increase the ion conductivity (Fig. 5).

The atomic fraction of the cation of interest (Li⁺ or Na⁺), which would have an influence on the C-rate capability, is ca. 5% (excl. H), close to the 8% for the system of Kubota. In comparison, polymeric single-ion conductors (SICs), with the same ion conduction mechanism, are often at ca. 1%, while
crystalline LISICON is at ca. 40%, but the conduction mechanism differs significantly.

From the above, Li[(TFSI)$_{0.6}$(MM$_{3411}$)$_{0.2}$] was selected for proof-of-concept of electrochemical stability tests. In the anodic part of the LSV, a two-step decomposition is observed (Fig. 7). The first step at 3.5 V vs Li$/\text{Li}^+$ is attributed to the decomposition of MM$_{3411}$, expected to have a lower oxidation potential than TFSI,\(^{20}\) while the second step, above 5 V vs Li$/\text{Li}^+$ likely corresponds to TFSI decomposition.\(^{33}\) Both steps are hard to resolve in the voltammogram as the current responses overlap. This can be attributed to the high electrolyte viscosity, resulting in slow diffusion of MM-anion decomposition by-products away from the electrode surface. The "tail" in the trace corresponds to a constant anion decomposition at the electrode surface. As compared to liquid LIB electrolytes a reduced slope of the small peak at ca. 0.6 V vs Li$/\text{Li}^+$ is attributed to the decomposition of Li$^+$/Li likely originating from Li$_2$CO$_3$ reduction and decomposition. This very low cathodic limit differs significantly from the reduction potential previously predicted for TFSI,\(^{34}\) likely due to a large polarization build up between working and counter electrodes in the experimental set-up.

On the cathodic side, due to the low electrolyte conductivity, the small peak at ca. 0 V vs Li$/\text{Li}^+$ is truly believed to correspond to minor lithium ion reduction and lithium metal plating, while the large feature below −2 V vs Li$/\text{Li}^+$ is due to TFSI anion reduction and decomposition. This very low cathodic limit differs significantly from the reduction potential previously predicted for TFSI,\(^{34}\) likely due to a large polarization build up between working and counter electrodes in the experimental set-up.

In conclusion, high purity and yield synthesis and full characterization of new Li/Na salts based on pseudo-delocalized anions (MM$_{nm11}$) was reported. Different combinations with LiTFSI were investigated as prospective battery electrolytes. The presence of 20–30 mol% of the MM$_{nm11}$ anions prevents completely crystallization, which proves the possible preparation at moderate temperatures (ca. 60 °C) of a liquid completely solvent-free electrolytes. The effect is more evident for the asymmetric MM$_{3411}$ anion as organized packing is further inhibited and opens for further exploring alternative flexible and bulky anions to form solvent-free battery electrolytes. Additionally, the presence of the bulky pseudo-delocalized MM$_{nm11}$ anions seems to have a positive effect on the Li$^+$ transference number. Apart from using the asymmetry of the MM$_{nm11}$ anions the ionic conductivity might be improved by reducing the ion–ion interaction further by replacing the −SO$_3^-$ moieties by more weakly cation coordinating units e.g. −SO$_2$−N−SO$_x$F$_y$, as already shown effective in block-co-polymer SICs.\(^{30}\)

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**