Multivalent Cation Transport in Polymer Electrolytes – Reflections on an Old Problem

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Today an unprecedented diversification is witnessed in battery technologies towards so-called post-Li batteries, which include both other monovalent (Na$^+$ or K$^+$) and multivalent ions (e.g., Mg^{2+} or Ca^{2+}). This development is driven, among other factors, by goals to establish more sustainable and cheaper raw material platforms, using more abundant raw material, while maintaining high energy densities. For these new technologies a decisive role falls to the electrolyte, that ultimately needs to form stable electrode-electrolyte interfaces and provide sufficient ionic conductivity, while guaranteeing high safety. The transport of metal-ions in a polymer matrix is studied extensively as solid electrolytes for battery applications, particularly for Li-ion batteries and are now also considered for multivalent systems. This poses a great challenge as ion transport in the solid becomes increasingly difficult for multivalent ions. Interestingly, this topic is a subject of interest for many years in the 80s and 90s and many of the problems then are still causing issues today. Owing to recent progress in this field new possibilities arise for multivalent ion transport in solid polymer electrolytes. For this reason, in this perspective a stroll down memory lane is taken, discuss current advancements and dare a peek into the future.

1. Introduction

Solid polymer electrolytes (SPEs) have a long tradition in battery research since the early works by Michel Armand in the 70s.[1,2] The class of ion-conducting polymers was quickly identified as potential solid electrolytes for intercalation compounds used in Li-ion batteries, particularly graphite.

Many research efforts have since focused on the development of fast Li-ion-conducting polymers, resulting in successful implementation into the Bolloré concept car (Bluecar)[3] first presented in 2006. The development of electrolytes for Li-ion technologies has also fostered the conceptual understanding of mono- and multivalent ion transport in polymer electrolytes and meanwhile research has gone far beyond Li-ions by covering nearly the full group of alkali metals and even multivalent cations of all sorts, such as Hg^{2+},[4] Pb^{2+},[5] or La^{3+}[6] to name a few of the more "exotic" examples.

In her book "Polymer Electrolytes"[7] Fiona M. Gray stated a growing interest in the late 1980s within the research community to study polymer electrolytes containing divalent or trivalent cations and further found that "multivalent systems still require fundamental research to clarify the types of applications that could be of practical consideration" and that due to the variety of multivalent cations their incorporation into suitable polymer hosts "could lead to a far wider diversity of properties than has been possible for monovalent systems". In fact, by expanding to multivalent systems a vast playground opened up to explore material properties and electrochemical characteristics. The field lay almost dormant for many years, at least with respect to materials for battery applications, until the advent of liquid-electrolyte-based (multivalent)

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post-Li battery technologies, mainly Mg-, Ca-, Zn- but also Al-based batteries.[8] With increasing interest in these multivalent ion battery systems, the scientific questions on suitable solid ion-conducting polymers is now back on the agenda. Since several "research generations" have actively worked in this area, it is now a good moment to revisit and bring back the relevant concepts and build a bridge to the current research activities. The considerable advancement in Li-battery materials, ion coordination and mechanistic understanding over the past two decades have also fostered new material developments for multivalent battery systems that now offer opportunities to cross-check previous findings but also conduct the experiments that have not been possible previously due to the lack of a suitable materials basis, for instance cell-level tests. Major roadblocks towards high-performing multivalent ion battery systems revolve around the following key challenges:

→ overcoming low ion mobilities, as a result of strong cation–host and cation–anion interactions, as well as polymer chain dynamics.
→ moving beyond poly(ethylene oxide) PEO host materials and advance to novel polymer structures and architectures.
→ enabling highly reversible electrode processes by removing sources of high charge-transfer and interfacial impedance.
→ mitigating electrolyte degradation at reactive electrode interfaces.

Two cations, namely magnesium (Mg^{2+}) and increasingly also calcium (Ca^{2+}), dominate the research landscape today as leading candidates for multivalent batteries. In the light of more diversification and sustainability of battery technologies, both Mg and Ca seem appealing, especially considering their high abundance for example. For Mg^{2+} and Na^+ similar concentrations in the earth's crust ($\approx$23 000 ppm) are found, for Ca the concentration is nearly twice as high than for the latter ($\approx$41 000 ppm)[9]. The electrochemical potential of Ca falls in the range between Li and Na ($E^0 = -2.87$ V vs SHE); that of Mg is somewhat lower ($E^0 = -2.37$ V vs SHE).[10] Owing to their high volumetric and gravimetric capacities as metallic electrodes they are attractive for high-energy batteries (**Figure 1**). The (Shannon) ionic radii of Mg^{2+} and Li^+ (72 pm vs 76 pm) and those of Ca^{2+} and Na^+ are similar (both 100 pm), but interesting differences in ion transport properties arise from their higher charge density and divalent character that influences coordination and solvation properties.[11] This perspective will focus on the developments of these two divalent cations that are in fact no strangers in the SPE domain. While the understanding in liquid electrolyte systems has made substantial progress in the past 10 years, especially towards Cl-free electrolytes, there still exist blank spots for corresponding SPE materials. For the discussions below results from liquid systems thus offer valuable lessons.

1.1. A Stroll Down Memory Lane

The variety of ions from main-group, transition metal and even rare earth elements that were studied as part of electrolyte salts in polymer electrolytes is far richer than the literature of the past
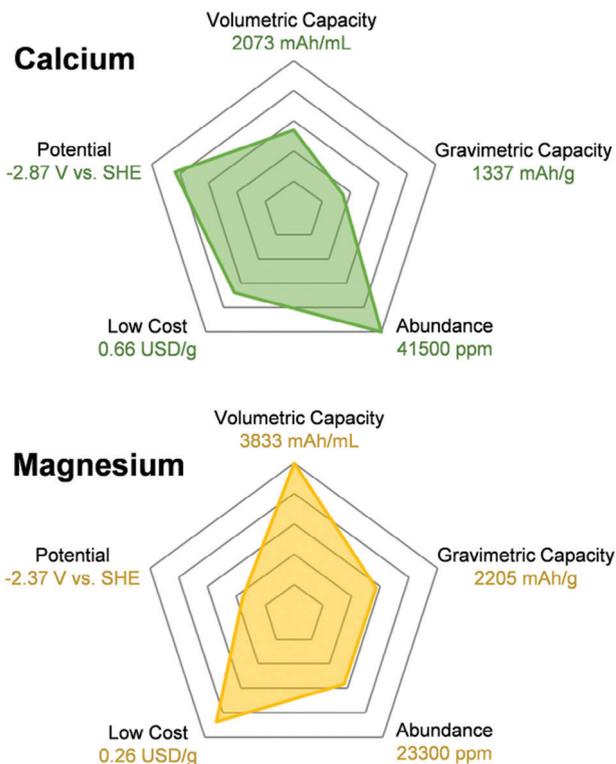

Figure 1. Performance indicators for Mg and Ca negative electrodes for multivalent metal-ion batteries. Adapted with permission.[9] Copyright 2020, Wiley-VCH.

20 years suggests. Di- and trivalent cations have been studied in the mid 80s and 90s by various research groups. According to Yang, McGhie and Farrington,[12] their initial work was motivated by the fact that ion conduction in PEO:LiX solid polymer electrolytes displayed a large fraction of anion conduction, i.e., a high anion transference number. The idea behind di- or trivalent cations was to immobilize the cation further and thus prepare dominantly anion conductors. Farrington and coworkers studied the ion conduction in $PEO:MgCl_2$[12] and $PEO:PbBr_2$,[13] showing that both salts form complexes over a wide range of compositions and moderate ion conduction at temperatures above 80 °C were measured that were in the same range as $PEO:LiCF_3SO_3$ salt mixtures ($\approx 10^{-6}$ to 10^{-5} S cm^{-1}). In a follow-up study, Huq and Farrington[14] pointed out that the cation transference numbers of $PEO:MgX_2$ complexes were close to zero (even at 100 °C), while polarizable ions like Pb^{2+} and Cd^{2+} displayed high transference numbers of up to $t_+ = 0.58$ (Pb^{2+}) and $t_+ = 0.92$ (Cd^{2+}), both at 140 °C. More importantly, the authors highlighted that a wide spread of transference numbers were reported in literature for different $PEO:MA_2$ systems (M = Zn, Cu, Ni, Cd; A = Cl, Br) that were skewed by the use of hydrated salts and improper drying. Without experimental details, the reported ionic conductivities in these early studies might thus be misleading in the context of battery research. Another early study by Fontanella et al.[15] reported on the ion conduction of alkaline earth thiocyanides ($Ca(SCN)_2$ and $Ba(SCN)_2$) in PEO by dielectric relaxation measurements in order to study the conductivity mechanism in PEO:salt complexes. The authors found comparatively
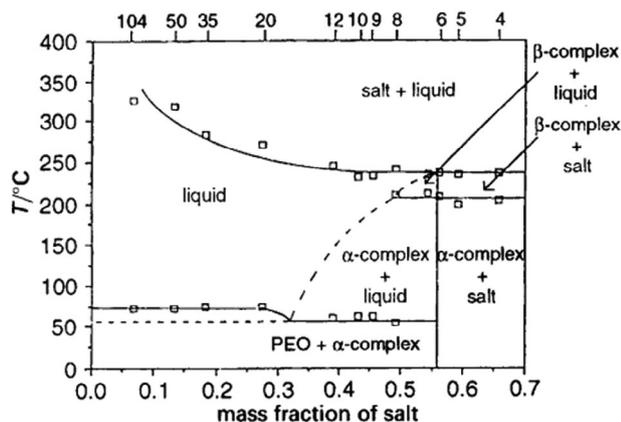
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Figure 2. Pseudo-equilibrium phase diagram of PEO:Ca(OTf)$_2$. Reprinted with permission.[19] Copyright 1993, American Chemical Society.

high glass transition temperatures of 35 °C (Ca^{2+}) and 55 °C (Ba^{2+}) with respect to monovalent systems and faster ion transport in PEO:Ba^{2+} (up to 10^{-6} S cm^{-1} at 100 °C) than PEO:Ca^{2+} (10^{-8} S cm^{-1}), presumably due to different PEO chain dynamics in dependence of cation radii and ion polarizability. Other studies on di- and trivalent cations used in PEO-salt complexes quickly followed, e.g. EuCl$_3$[16,17] the perchlorates La(ClO$_4$)$_3$,[6] A(ClO$_4$)$_2$ (A = Mg, Ca, Sr)[18] and Hg(ClO$_4$)$_2$,[4] as well as various triflates (CF$_3$SO$_3^-$, OTf) of Ni, Zn, Pb, or Ca,[5,19] to name but a few. Furthermore, Mehta et al.[19] was first to publish the phase diagram of the PEO:Ca(OTf)$_2$ system which is a useful resource to assess thermal properties (refer to **Figure 2**). In the year 2000 Aurbach et al.[20] reported a Mg-ion battery prototype based on organometallic Grignard-containing electrolyte in low-molecular ether solvents. Only one year later, a patented work by Di Noto and Fauri[21] demonstrated that oligomeric Mg-poly(ethylene glycol) complexes, PEG:(δ-MgCl$_2$)$_n$ offer a safe alternative to rechargeable magnesium batteries.

1.2. Conceptional Understanding

Bruce, Kork and Vincent distinguished two types of PEO:salt complexes, based on the observed mobility in strictly anhydrous polymer electrolytes based on the cation transference numbers[4]: 1) t_+ is virtually zero, e.g. for PEO:MgCl$_2$ or PEO:ZnBr$_2$ and 2) $t_+ > 0$, which includes systems with significant cation mobility, e.g. PEO:CdBr$_2$ and PEO:PbBr$_2$. The authors identified three decisive parameters that determine the cation mobility:

(a) Strong cation–solvent interactions that allow the electrolyte salt to dissolve in the polymer matrix, i.e., to overcome its lattice energy.

(b) As a result of a), salts with a small lattice energy are favorable, as solvation is achieved easier.

(c) Bond lability, i.e., facile coordinate bond formation and breaking between cation and polymer ligand.

Complexation of metal ions by (multi-dentate) polymer ligands may generally lead to thermodynamically stable complexes,

but kinetically many are considered labile. This is expressed in the ligand exchange rate that can vary over many orders of magnitudes for metal ions of the same valency.[11] The dynamic character of coordinate metal-ligand bonding means continuous change of the coordination environment around the metal ion, thus allowing its transport in a polymer matrix. In other words, for high ion mobility rapid ligand exchange rates are prerequisite; vice versa complexes that are kinetically inert (low exchange rates) are associated with poor transport properties. At the same time sufficient coordination strength is desired to dissolve the electrolyte salt, i.e., to achieve solvent-separated ion pairs. These two parameters are not necessarily contradicting, as will be shown in the following section.

For the coordination strength, the hard–soft acid–base (HSAB)[22] principle can give a first rule of thumb to assess if cations interact strongly with electron donors, such as anions or the ether oxygens in PEO. For instance, the hard Lewis acidic Mg^{2+}-ions will interact strongly with the also hard Lewis basic ether oxygens (EO), as opposed to interactions between the soft Lewis acidic Hg^{2+}-ions with hard Lewis basic EO. Similarly, replacing PEO by a thioether could reverse the situation. It should be highlighted that the notion of "weak" and "strong" is relative in this comparison, as the typical polymer ligands discussed herein are weak σ-donor ligands.

For alkali and alkaline earth ions, their surface charge density and coordination number are the prime parameters in this consideration. Coordinate bonds can be weakened by larger coordination numbers (CNr) as the polymer conformation adapts to different cations sizes, as it has been observed for example in a comparison between PEO:LiOTf and PEO:KSCN or PEO:RbSCN complexes[23]. To the best of our knowledge, similar in-depth structural XRD studies as in ref.[23] are not reported for PEO-complexes with multivalent cations, with exception of the Ca(OTf)$_2$ system.[19] However, detailed Fourier-transform infrared (FTIR) spectroscopy studies by Bakker et al.[24] show interesting trends among the group of alkaline earth metals, demonstrating that the EO:A[N(CF$_3$SO$_2$)$_2$]$_2$ (A = Mg, Ca, Sr, Ba) interactions decrease with increasing cation size, which in turn favors ion pairing in course of increased anion-cation attractive forces for larger cations. In addition, the authors concluded that the Mg^{2+}-CNr could be smaller than six (the most common CNr for Mg^{2+} in aqueous systems and crystalline hydrates), based on excess, non-coordinated ether-oxygens in a EO:Mg^{2+} = 6:1 mixture.[24] For transition metals with their d-orbital interactions and different coordination geometries, assessing the coordination strength becomes more complex. Similarly, lanthanides show different behavior as a result of d–f-orbital interactions (see below).

Ionic conductivities of PEO complexes with multivalent electrolyte salts were studied intensively and found to vary to significant degrees. One of the root causes was the drying process after casting the polymer films and the use of hydrated or anhydrous electrolyte salts. Huq et al.[14] grouped electrolytes of divalent cations dissolved in PEO into three categories:

i. pure anion conductors.
ii. electrolytes with significant cation transfer numbers.
iii. "activated" electrolytes by controlled hydration.

Table 1. Examples on the cation transport in PEO:AX2 polymer electrolytes in dehydrated and "controlled hydrated" conditions.

Composition	EO:A+	Hydrated/ dehydrated	t_+	Temp. [°C]	Ref.
PEO:MgCl$_2$	16:1	Dehydrated	>0.005	100	[12]
PEO:Mg(ClO$_4$)$_2$	16:1	Dehydrated	>0.005	100	[25]
PEO:Mg(ClO$_4$)$_2$	16:1	Hydrated	>0.005	100	[18]
PEO:NiBr$_2$	8:1	Dehydrated	0.09	140	[14,26]
PEO:NiBr$_2$	8:1	Hydrated	0.6	140	[14,26]

Hard, poorly polarizable cations, such as Mg^{2+} and Zn^{2+}, in dehydrated electrolytes tend to be entrapped in the polymer matrix due to strong electrostatic cation–EO interactions. Thus, ionic conductivity in category i) originates mainly from anion mobility. Category ii) refers to softer, polarizable cations, typically those with higher ionic radii like Pb^{2+} or Cd^{2+}, that show much weaker interactions with the polymer chain and thus show dominant cation transport (i.e., high cation transference numbers) at higher temperatures (above 100 °C). Coordination numbers for large cations (e.g., Pb^{2+}) can be up to CNr=8–10 and thus interact with a larger number of polymer repeating units. As a result, they are less tightly associated with the polymer than smaller cations in a crown-ether-type coordination.[9] The third category iii), refers to electrolytes prepared with hydrated salts that would otherwise act predominantly as anion conductors ($t_+ \approx 0$). Thus, controlled moisture levels significantly increased the cation transport number, as outlined for some early works in **Table 1**.

2. Roadblocks for Multivalent Ion Transport in Polymers

2.1. Polymer Electrolytes for Multivalent Cations

In this first section, focus will be placed on the material aspects, specifically polymer architecture and electrolyte salts. The working horse PEO plays traditionally a vital role in this discussion. **Table 2** summarizes studies on PEO-based electrolytes for applications in Mg-based batteries and their corresponding ionic conductivities. **Table 3** provides an overview of recent studies that diversified in the choice of the polymer host ("beyond PEO"[27]). Tables 2 and 3 are not intended as exhaustive reviews but rather as an illustration of the latest representative developments in this field (a more comprehensive summary for Mg-SPEs is provided by ref.[28]). For the emerging class of Ca-SPEs **Table 4** provides additional information. Because of various conventions in reporting salt concentrations (e.g., mol.%, wt.% or EO:A^{n+} ratio; sometimes not clearly stated at all), as well as lack of consistency on reporting ionic conductivities data and corresponding temperature, direct comparisons between different studies are often challenging. Many data points could only be approximated from graphs in the respective publications.

Table 2. Selected publications on the performance of PEO-based SPEs with various types of Mg-salts.

Polymer host	Mg salt	Salt conc. [wt.%]	Filler	Temp. [°C]	σ [S cm^{-1}]	Ref.
PEO	Mg(ClO$_4$)$_2$	2		r.t.	4.4×10^{-8}	[29,31]
		15		r.t.	1.4×10^{-6}	
				75	1.1×10^{-3}	
PEG400	δ-MgCl$_2$	14.2		r.t.	1.9×10^{-3}	[35]
PEO	Mg(NO$_3$)$_2$	20		30	1.3×10^{-5}	[30]
PEO	Mg(TFSI)$_2$	26		r.t.	1.6×10^{-9}	[34]
				50	1.8×10^{-7}	
PEO	Mg(TFSI)$_2$	8, 12, 16, 20, 28, 36		80	10^{-3}–10^{-4}	[33]
PEO	Mg(OAc)$_2$	15	CeO$_2$	30	3.4×10^{-6}	[63]
PEO	Mg(OAc)$_2$	15	TiO$_2$	30	5.0×10^{-5}	[64]
PEO	Mg(ClO$_4$)$_2$	10	Al$_2$O$_3$	r.t.	$\approx 10^{-5}$	[50]
PEO	MgCl$_2$	20	B$_2$O$_3$	30	7.2×10^{-6}	[65]
PEO	Mg(OTf)$_2$	20	TiO$_2$	r.t.	1.7×10^{-5}	[53]
			SiO$_2$		5.9×10^{-6}	

2.1.1. Limitations of Mg^{2+} Transport in PEO Electrolytes

Currently, only a limited amount of research on multivalent ion-conducting SPEs has been conducted and has mainly focused on Mg-conducting polymer electrolytes. As outlined in the introduction, the early stages of SPE development on Mg electrolytes were very much driven by the development of Li-SPE thus leading to a strong focus on PEO[12,18,24,29–31] as the polymer matrix (Table 2). PEO has been widely investigated for different types of SPEs and is often utilized in SPE development due to its ability to easily

Table 3. Selected publications on the performance of SPEs with various types of Mg-salts and alternative polymer hosts (not exhaustive).

Polymer host	Mg salt	Salt conc. [wt.%]	Temp. [°C]	σ [S c^{-1}]	Ref.
PEC	Mg(ClO$_4$)$_2$	45.5	90	5.2×10^{-5}	[62]
	Mg(TFSI)$_2$	45.5	90	6.0×10^{-6}	
P(BEC)	Mg(TFSI)$_2$	5	20	2.7×10^{-7}	[66]
	Mg[B(hfip)$_4$]$_2$	40	20	9.2×10^{-8}	
PCL-PTMC	Mg(TFSI)$_2$	28	r.t.	2.52×10^{-8}	[33]
Pectin	Mg(NO$_3$)$_2$	50	r.t.	7.7×10^{-4}	[67]
Pectin	MgCl$_2$	70	r.t.	1.4×10^{-3}	[61]
Cellulose acetate	Mg(NO$_3$)$_2$	40	r.t.	9.19×10^{-4}	[68]
Cellulose acetate	Mg(ClO$_4$)$_2$	40	r.t.	7.79×10^{-4}	[69]
Methyl cellulose	Mg(NO$_3$)$_2$	25	r.t.	1.02×10^{-4}	[70]
Chitosan	Mg(OTf)$_2$	50	r.t.	9.58×10^{-5}	[71]
Agar	Mg(OTf)$_2$	30	30	1.0×10^{-6}	[72]
			70	3.8×10^{-6}	
P(VdCl-co-AN-co-MMA)	Mg(NO$_3$)$_2$	30	r.t.	1.6×10^{-4}	[73]
P(VdCl-co-AN-co-MMA)	MgCl$_2$	30	r.t.	1.89×10^{-5}	[74]

Table 4. Ionic conductivity of Ca2+ polymer electrolytes.

Polymer	Salt	EO:Ca²⁺ ratio	Temp. [°C]	σ [S cm⁻¹]	Ref.
PEO	Ca(OTf)₂	8	90	2.3×10^{-4}	[77]
		30	90	4.7×10^{-4}	
PEGDA	Ca(NO₃)₂·4H₂O	5	110	3.4×10^{-4}	[79]
		5	r.t.	3.0×10^{-6}	
Agarose	Ca(SCN)₂	40 wt.%[b]	r.t.	8.01×10^{-5}	[80]
		45 wt.%[b]	r.t.	2.28×10^{-4}	
PVA/PVP	CaCl₂	15 wt.%[b]	90	1.70×10^{-4}	[81]
PTHF—Epoxy	Ca(NO₃)₂	1.9	30	1.26×10^{-4}	[82]
		1.9	110	1.57×10^{-2}	
PTHFDA-STFSI[a]	Single-ion-conducting		85	3.5×10^{-13}	[83]
			25	7.0×10^{-6}	
Polyvinylimid-azole[a]	Ca(TFSI)₂	1.0 м[c]	r.t.	5.4×10^{-4}	[84]
		0.5 м[c]	r.t.	1.26×10^{-3}	
PEGDA[a]	Ca(ClO₄)₂	≈10	r.t.	1.74×10^{-4}	[85]
		≈10	110	2.21×10^{-3}	

[a] Sample at 25 °C was a GPE with TEG as solvent; measurement at 85 °C refers to dry polymer;[83]   [b] Salt concentration in weight percent due to absence of EO units; [c] Polymer was polymerized in a solution of the specified salt concentration.

dissociate metal salts and its low glass transition temperature, of ≈−56 °C to −52 °C[32], allowing high degrees of polymer dynamics and thus leading to good ionic mobility. PEO displays good thermal and electrochemical stability and enables formation of flexible polymer films even without additives. Especially regarding SPE preparation, PEO stands out owing to its solubility in a wide range of solvents, allowing for flexibility in SPE preparation by solvent casting. Because of these advantages, PEO has usually been the first choice for initial studies.

Early examples were mainly limited to Mg-salts such as MgCl₂,[12] Mg(ClO₄)₂,[18] Mg(NO₃)₂,[30] and Mg(TFSI)₂[24] and produced SPEs with ionic conductivities of up to 1.34×10^{-5} S cm⁻¹ at 30 °C for Mg(NO₃)₂[30] (Table 2). As mentioned in the previous section, different drying conditions play a very important role in the measured values and vastly different transport properties in multivalent systems. Newer studies suggest that the ionic conductivities in these early stud-

ies were overestimated, as seen in two recent studies by Park et al.[33] and Walke et al.[34] Both studies found significantly decreased glass transition temperatures between −30 °C and −20 °C for low and intermediate salt concentrations between 10–40 wt.%, which was explained by stronger ionic cross-linking effects, as compared to monovalent cations. Just above the melting temperature (estimated to 50–65 °C from **Figure 3**), (total) ionic conductivities reached the 10⁻⁴ S cm⁻¹ regime. It is important to stress that the contribution of Mg²⁺-ions to σ is unclear, for reasons further discussed below. Even at the highest salt concentration in these studies, the Mg(TFSI)₂ was fully dissociated to a large degree (>90%), as determined from vibrational spectroscopy.[33]

It is further worth stressing out that the use of oligomeric, i.e., low-molecular weight PEO (also named PEG), in combination with δ-MgCl₂ (see above) improved the room temperature conductivity compared to (PEO)₈:MgCl₂ (i.e., high-molecular PEO) by several orders of magnitude to a value of 1.9×10^{-5} S cm⁻¹.[35] The use of disordered δ-MgCl₂[36] allowed higher salt contents of up to 15 wt.% in the polymer-salt complex, which the authors associated to its unique polymeric structure. Based on results from impedance spectroscopy and GHz broadband electrical spectroscopy several conduction pathways exist in which Mg²⁺ and [MgCl]⁺ cations are transported by ion-hopping between coordination sites as well as migration along PEG chains.[37,38] As the materials tend to exhibit (ionic) liquid-like properties,[39] it was suggested to reinforce the electrolyte matrix with glass fibers.[21]

Addition of Inorganic Fillers: For further improvements PEO-based SPEs were blended by various oxide nanoparticles as inorganic fillers to create composite SPEs (refer to Table 2). Inorganic fillers, have been shown some success for Li- and Na-SPEs in lowering the PEO crystallinity,[40] improving mechanical properties[41] and increase cation transport by Lewis-acid-base interactions between particle and polymer.[42–45] Confinement effect of the polymer chain movement along the particle interface can occur,[46,47] which would be reflected in increasing T_g values. This may create conducting pathways for ions to move more freely in the particle-polymer interface region. The extend of this effect also depends on factors like filler's particle size, distribution as well as content in the composite.[43,45,48,49] For Mg-PEO composites the main research focus was on MgO and Al₂O₃ fillers which led to significant improvements, as first
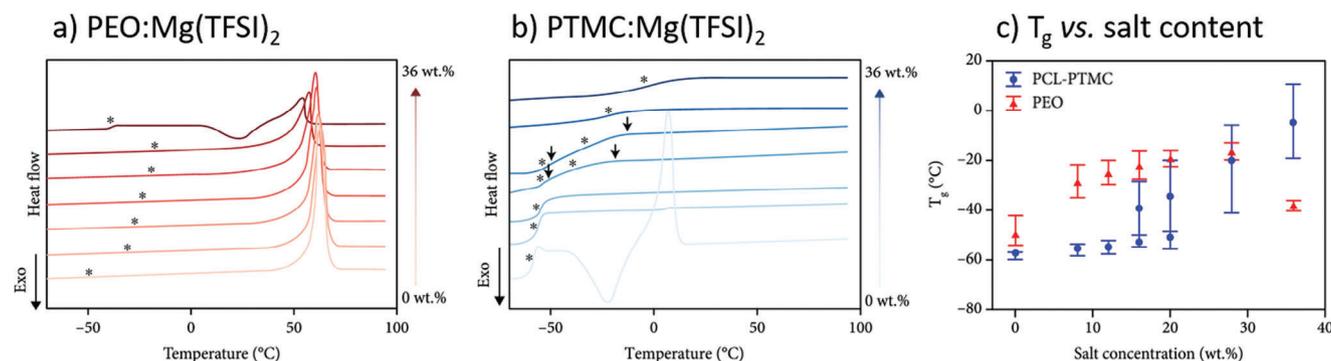

Figure 3. Thermal properties determined by differential scanning calorimetry (DSC) of PEO:Mg(TFSI)₂ a) and PTMC:Mg(TFSI)₂ b) compositions. The evolution of the glass transition temperature (T_g) as a function of salt concentration is presented in c). Adapted with permission.[33] Copyright 2021, Park et al.

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demonstrated by Dissanayake et al.,[50] who could show an increase of the ionic conductivity of PEO:Mg(ClO$_4$)$_2$ by an order of magnitude. This conductivity improvement was associated with new ionic conduction pathways at the Al$_2$O$_3$–particle interface. However, it was shown that the improvement of ionic conductivity was mostly due to improved anionic mobility similar to findings in gel polymer electrolytes,[51] which underlines the importance of testing SPEs electrochemically to demonstrate cation mobility and possibly lower overpotentials related to mass transport in a practical manner. This approach was chosen by Shao et al.,[52] who recently reported stable magnesium plating/stripping from a solid composite polymer electrolyte using MgO as inorganic filler. However, Mg-deposition was observed only when Mg(BH$_4$)$_2$ was utilized as electrolyte salt, while the application of Mg(TFSI)$_2$ did not allow for reversible Mg-deposition.

This is interesting to highlight for two reasons: 1) it could be necessary for multivalent ion transport to reconsider the choice of electrolyte salt, which is still strongly influenced by the Li-SPE field (see also discussion below); and 2) as will be discussed in more detail in Section 2.3, the BH$_4$-anion was reported to activate alkaline earth metal electrodes and facilitate the deposition process. Agrawal et al. systematically examined the influence of different filler types.[53] Out of the three studied materials MgO, TiO$_2$ and SiO$_2$, the highest improvement of ionic conductivity was achieved with MgO particles. It was also reported that the particle size plays a significant role, as the nanoscale material performed significantly better, as composites with more than double the ionic conductivity (1.67×10^{-5} S cm^{-1}) were obtained in comparison to composites from micro particles (6.91×10^{-6} S cm^{-1}).

Despite the notable improvements of PEO-based SPEs, e.g., by addition of fillers and the change to boron-based salts, there appear to be limitations to their transport properties with respect to practical applications. For this reason, alternative polymer hosts have emerged with the aim to further advance Mg^{2+} transport, as will be discussed in the next section.

2.1.2. Mg Polymer Electrolytes Beyond PEO

In Table 3 an overview of recent works is provided that looked beyond the use of PEO. In following the most prominent examples will be discussed.

Poly(vinyl alcohol) (PVA) can be solubilized in water and shows a high melting point and glass transition temperature of 228 °C[54] and ca. 85 °C respectively. The high glass transition temperature of PVA indicates low chain mobility at lower temperature. However, high ionic conductivities have been reported nonetheless, even at room temperature. It is worth noting that solvent residues from the film casting process often lead to solvent-ion complexes with notably higher conductivities than a fully dried SPE (which is a challenge in itself for PVA to prepare).[55,56] This also holds true for many biopolymers.

The good mechanical properties of PVA have also led to its application as part of polymer blends with different polymers such as *polyacrylonitrile (PAN)* to ensure sufficient flexibility of the resulting electrolyte.[57–59] For these polymer blends, high ionic conductivities in the range of 10^{-3} to 10^{-4} S cm^{-1} at 30 °C with Mg(ClO$_4$)$_2$, MgCl$_2$ or Mg(NO$_3$)$_2$ have been reported. Neverthe-

less, there are to date no reports of reversible plating/stripping from PVA-based SPEs and only primary Mg-battery results have so far been reported. This raises compatibility questions between the Mg-metal anode and the PVA's hydroxyl group content, that has already been suspected to lead to anode passivation.[28] In addition, for PVA-based electrolytes, the content of remaining poly(vinyl acetate) (PVAc) has to be considered, as PVA is produced by hydrolysis of PVAc. However, the degree of hydrolysis is rarely reported.

Biopolymer-based electrolytes have some similarities to PVA with regards to their degree of substitution that might also become an issue as post-modification reactions seldom reach full conversion, leaving behind residual and reactive functional groups, such as hydroxyl groups. Acidic protons in contact with the negative electrode lead to H$_2$ gassing.[60] Also in regards to SPE preparation biopolymers are similar to PVA as they are mostly soluble in water and DMSO, which are difficult to remove,[55] as it has been shown that the ionic conductivity for PVA:LiTFSI SPE, is strongly influenced by residual solvent content.[56] It was generally observed that the biopolymers listed in Table 3, exhibited exceptionally high room temperature ionic conductivities, for example for the Pectin:MgCl$_2$ based electrolyte (1.4×10^{-3} S cm^{-1} [61]). The spread in ionic conductivity between "classic" polymer materials is comparatively high (Table 3). Such ionic conductivities are usually not even achieved in SPEs comprising monovalent cations. Developing better understanding of the governing ion transport mechanisms could thus be relevant for future SPE design. Furthermore, the impact of residual solvent contents should be critically reviewed. In this context, developing new processing methods for these types of materials could be considered. In addition, results could be supported by conducting the final evaluation of novel electrolyte materials in cell tests either by demonstrating reversible plating and stripping experiments or in Mg-battery full cell setups.

Polycarbonates seemingly hold promise for the development of SPEs, due to their high mechanical flexibility and thermal stability in the absence of hydroxyl groups. The research on poly carbonates was spearheaded by Ab Aziz and Tominaga who reported a poly(ethylene carbonate) (PEC)-based SPE with either Mg(TFSI)$_2$ or Mg(ClO$_4$)$_2$ as conductive salts.[62] They demonstrated the ability of PEC to dissociate Mg-salts and the occurrence of Mg-ion conduction. However, the ionic conductivity stayed low at 10^{-5} S cm^{-1} even at 90 °C and only Mg(TFSI)$_2$ showed cathodic and anodic current peaks in CV experiments.

Further, comparative studies between PEO and *poly(ϵ-caprolactone-co-trimethylene carbonate)* (PCL-PTMC) have been conducted by Park et al.,[33] demonstrating that the PCL-PTMC copolymer showed different temperature dependence and about two orders of magnitude lower ionic conductivities. In addition, the authors showed a weaker coordination, i.e., more ion pairing, in comparison to PEO. Reversible plating/stripping could not be achieved due to passivation of the Mg-anode, which was caused by TFSI decomposition products (Section 2.3). Using poly(2-butyl-2-ethyltrimethylene carbonate) with either Mg(TFSI)$_2$ or Mg[B(hfip)$_4$]$_2$ salts Sundermann et al.[66] were first to report the application Mg-borate salts, leading to an ionic conductivity of 2.5×10^{-4} S cm^{-1} at 120 °C for a polymer-in-salt electrolyte formulation with a high stability window of up to 6 V

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versus Mg^{2+}/Mg. The results of SPEs using the borate salt exceeded those of the commonly used $Mg(TFSI)_2$ salt. However, even in the $Mg[B(hfip)_4]_2$-containing SPE, no long-term plating/stripping could be achieved. This suggests that the challenges of Mg-SPEs cannot be overcome solely by new approaches in polymer design and application of new generation Mg-salts, but instead needs to be paired with interface design strategies.

Poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate), p(VdCl-*co*-AN-*co*-MMA) is another example of a copolymer employed for Mg-SPEs, reported by Ponraj et al.[73,74] SPEs based on P(VdCl-*co*-AN-*co*-MMA) either $MgCl_2$ or $Mg(NO_3)_2$ showed a relatively high ionic conductivity of 1.89×10^{-5} and 1.6×10^{-4} S cm^{-1}, respectively, at room temperature, thereby highlighting the potential of new polymer architectures.

Aside from the discussed polymer classes, different polymer blends and some single-ion conductors have been investigated.[28] However, in our opinion it is difficult to extrapolate a clear trend in regards to the fundamentals of multivalent ion conduction from these studies.

2.1.3. Polymer Electrolytes for Ca^{2+}

Though in an early stage, recent progress in the development of calcium-ion batteries has also motivated studies on SPEs for Ca^{2+}. Because of the high reactivity of Ca metal, liquid electrolytes tend to decompose readily, passivates the Ca metal interface and hinders Ca^{2+} plating.[75,76] In this regard, polymer electrolytes are of great interest as they can potentially provide more stable SEIs and improve Ca^{2+} plating/stripping.

To summarize the recent progress in the area, ionic conductivities of different polymers compositions are collected in Table 4. Polymer electrolytes for Ca-metal batteries may be divided into two groups: solid-state polymer electrolytes and gel polymer electrolytes as labeled in Table 4. The most intensively studied polymer electrolyte for solid-state Ca^{2+} battery applications is also PEO. Martinez-Cisneros et al.[77] investigated the ionic conductivity of linear PEO with different Ca^{2+} salts for use as SPEs in battery applications, such as: $(Ca(CF_3SO_3)_2, CaI_2, $ and $Ca(TFSI)_2)$. The authors showed that the ionic conductivity of PEO in the semi-crystalline state is rather low. With an increase of temperature over the melting point of PEO, good conductivity can be achieved above 90 °C (up to 4.7×10^{-4} S cm^{-1}). Increasing the concentration of $Ca(OTf)_2$ does not lead to better conductivity, likely because increasing the salt concentration increases the ratio of ion pairs and aggregates and thus reduces the ratio of free ions.[78] However, after melting of crystalline domains in PEO, the storage modulus drops significantly, leading to creeping phenomena at temperatures $T \geq 80$ °C. Therefore, Genier and colleagues improved the mechanical stability of the polymer electrolyte, by utilizing cross-linked poly(ethylene glycol) diacrylate (PEGDA).[79] Although crystallinity was suppressed, and better thermal properties were achieved in comparison to linear PEO, the ionic conductivity at 90 °C was an order of magnitude lower. One of the reasons, could be the use of the less suitable $Ca(NO_3)_2$ salt in high concentration. Depending on Ca^{2+} salt concentration, the T_g of cross-linked PEGDA reaches 78.6 °C at an EO:Ca ratio of 5:1. According to DSC and XRD measurements, polymerized PEGDA / Ca salt compositions are amorphous.

Nevertheless, these compositions still possess a low ionic conductivity of 3.0×10^{-6} S cm^{-1} at room temperature.

Therefore, in subsequent studies, ionic liquids (ILs)[85] and liquid electrolytes[86] were added to the composition of PEGDA and Ca^{2+} salt to form gel-polymer-electrolytes (GPEs). In general, GPEs deliver better ionic conductivity and improved contact with electrodes in comparison to SPEs.[87] This strategy has been leveraged successfully to build a Ca-ion battery based on a $Ca_3Co_4O_9$ negative and a V_2O_5 positive electrode, as well as a PEGDA-IL gel polymer electrolyte that performed over 25 cycles at room temperature. Wang et al. copolymerized polytetrahydrofuran (PTHF) with a cycloaliphatic epoxy and $Ca(NO_3)_2$.[82] These compositions showed promising ionic conductivities reaching 1.57×10^{-2} S cm^{-1} at 110 °C, but a thermal stability merely up to 120 °C. In a recent paper, Pathreeker and Hosein proposed vinylimidazole-based gel polymer electrolytes as an alternative to oxygen-based coordination chemistries for improved cation transport.[84] They polymerized vinylimidazole in the presence of $Ca(TFSI)_2$ and obtained a gel electrolyte comprising a poly(vinyl imidazole) host infused with liquid vinylimidazole. Furthermore, polymer blends[81] and biopolymers[80] were also studied as SPEs for Ca^{2+}. For example, Ford et al.[83] developed a single-ion conducting polymer for Ca^{2+} transport by copolymerizing polytetrahydrofuran diacrylate with 4-styrenesulfonyl (TFSI)imide (PTHFDA-STFSI) resulting in a cross-linked network. These SPEs were able to conduct Ca^{2+}, but displayed poor ionic conductivities. Therefore, EC:PC solution was employed to prepare GPEs in order to increase the ionic conductivity to a value of 7.0×10^{-6} S cm^{-1} at 25 °C.

In summary, GPEs seem currently as the most promising strategy for room temperature Ca-ion batteries, owing to their higher ionic conductivity as a result of ion transport in the liquid phase. For purely solid polymer electrolytes, research is just at the beginning and most studies have so far been focusing on polyether-based systems. While this serves as a good basis for future studies, there is a larger variety of potential candidates available, as the developments of Mg-SPEs has shown (Tables 2 and 3). Besides the development of new polymer hosts, further studies on the cycling performance of Ca^{2+} polymer electrolytes are of great interest for the future development of this new battery technology.

2.1.4. Electrolyte Salts for Multivalent Systems

As the research on liquid electrolytes has shown, the choice of electrolyte salts in multivalent systems faces profoundly new challenges, which is a problem that is strongly associated with ion association and electrochemical stability.

Organometallic Compounds: Magnesium organohaloaluminates are the products of Lewis-acid-base reactions between organo-magnesium (R_2Mg) and organo-halo aluminium compounds (AlR_nCl_{3-n}) that may form stoichiometric complexes of the general composition $Mg(AlCl_{4-n}R_n)_2$.[20] The electrolyte salts are soluble in ether solvents (specifically THF) and show exceptionally high plating and stripping efficiencies.[88] In order to increase the stability window (>3.3 V) and reduce β-H elimination of the alkyl groups at the Al centers, phenyl complexes were proposed, based on PhMgCl and $AlCl_3$ as starting materials.[89]

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For polymer electrolytes this class of salts has so far not played a significant role, which is likely due to the expected reactivity between salt and polymer (as the organometallic reagents are widely classified as pyrophoric[90]). Moreover, corresponding Ca-compounds have so far not been identified.[91]

Halides: Magnesium and aluminium halides are widely known to form Lewis-acid-base combinations to form binuclear/dimer or chain-like structures, such as $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ or Al_2Cl_6 dimers.[92] The solubility of $MgCl_2$ in glyme solvents is limited (fluorides are essentially insoluble). According to Shterenberg et al.[93] the solubility of $MgCl_2$ was only 0.25 M, which can be extended when $MgCl_2$ is converted into $\delta\text{-}MgCl_2$.[35] The resulting PEG:($\delta\text{-}MgCl_2$) electrolyte mixtures were the basis for a rechargeable Mg-battery patented in 2001.[21] Despite the complex dissociation equilibria and the possible limitations in solubility, a major concern with the use of halide-containing electrolyte salts (including Grignard reagents) for solid or ionic liquid electrolytes is pitting corrosion of stainless steel, Al current collectors[94–96] and even transition metal oxides. Therefore, today's research activities are shifting towards halide-free electrolyte salts, even though halide salts remain part of the research landscape, as show in Tables 3 and 4.

Perchlorates: Although commonly encountered in monovalent SPEs, perchlorates are expected to be highly reactive with Mg- or Ca-metal and tend to form inhibiting surface oxides.[88,97] Although, Ca-deposition from carbonate solvents was reported at elevated temperatures, the reversibility was poor.[10] More importantly, reversible stripping/plating could not be achieved in PEC:Mg(ClO₄) electrolytes under similar conditions, which the authors referred to the formation of ionic clusters.[62]

Triflimidates: The use of *trifluoromethane sulfonate* (triflate) salts ($A^{n+}(CF_3SO_3)_n$; OTf) were commonly used in early studies, e.g. for a structural analysis and construction of a phase diagram for PEO:Ca(OTf)₂ (Figure 2) reported by Mehta et al.[19] It was further reported that the mixtures of PEO and triflate salts of divalent earth alkali metals (A/EO ratios <9) yielded highly crystalline salt complexes that are stable beyond the melting point of PEO. Fully amorphous complexes were obtained at a temperature of 204 °C.[98] In contrast, Bakker et al.[24] found fully amorphous PEO complexes for A:EO≤16 for the bis(trifluoromethane)sulfonimide (TFSI) salts of alkaline earth metals (M = Mg, Ca, Sr, Ba). In fact, the TFSI-anion is a popular choice in SPE studies, as a bulky non-coordinating anion that enables higher ion mobility as well as reduced polymer crystallinity and enhances chain mobility through plasticizing effects. For multivalent ions however, the use of TFSI-salts is associated with a number of challenges related to its cathodic stability towards earth alkaline metal electrodes in certain coordination environments (Section 2.3). Interestingly, the addition of $MgCl_2$ to $Mg(TFSI)_2$ containing electrolytes in ether solvents greatly improved the electrochemical properties and also doubled the solubility of $MgCl_2$ over a neat solution of the halide in the respective ether.[93]

Borates: *Tetrahydroborates* (BH_4^-) plays an intriguing role in Mg- and Ca-battery electrolytes, as it was among the first halide-free salt reported to allow repeated plating and stripping on metallic Mg[99] and Ca[75] electrodes at room temperature. The role of the salt is manifold, as it acts both as an effective drying agent[100] and affects the deposition process as well[101] (see

Section 2.3). Similar as Al- or Mg-chlorides, BH_4^--salts tend to form μ-hydride-bridged complexes,[102] causing strong ion association and poor solubility. As it turns out, glymes are most suitable to separate the contact ion pairs. Mohtadi et al.[75,99] further demonstrated that addition of LiBH₄ increased the degree of dissociation as well. In contrast, $Ca(BH_4)_2$ shows more benign dissociation properties also in ether solvents. Another commonly used borate salt is *tetrafluoroborate (BF_4^-)* that has been shown to allow Ca-deposition at elevated temperatures from ether solvents.[10] However, significant amounts of CaF_2 also deposited on the Ca-metal surface, in course of side reactions.[103] Ponrouch and coworkers[76] also reported on reversible stripping and plating in a $Ca(TFSI)_2$ electrolyte, if the Ca-metal is pretreated with a solution of $Ca(BF_4)_2$. An interesting alternative to the commonly used borate salts above are salts based on the *tetrakis(hexafluoroisopropyloxy)-borate* anion $[B(hfip)_4]^-$.[92] The magnesium salt $Mg[B(hfip)_4]_2$ was first reported by Zhao-Karger et al. in 2017 and showed an exceptional stability towards air and moisture, high anodic (up to 4.3 V vs Mg/Mg^{2+} for stainless steel (SS316L) and Al substrates) and cathodic stability and well reversible plating/stripping behavior. Similarly, the corresponding calcium salt, $Ca[B(hfip)_4]_2$, showed equally promising behavior with respect to chemical stability and reversible plating/stripping behavior.[103,104] It should be further highlighted that fluorinated alkoxyborates represent a broader class of possible electrolyte salts, of which so far focus has been mainly placed on hfip. Alternative borate ligands also include the recently reported bidentate *fluorinated pinacolatoborate $[B(O_2C_2(CF_3)_4)_2]^-$* for Mg-electrolytes.[105] In its nature the anion resembles the bis(oxalato)borate (BOB) anion that is increasingly used in Li-ion battery electrolytes.[106] An example for an entirely fluoride-free borate is *tetraphenylborate* (BPh_4^-) that was recently used in K-ion batteries.[107]

2.1.5. Cation Coordination in Ethers

For both Ca and Mg the commonly reported CNr is 6.[91] However, as shown in recent crystallographic studies on electrolyte salt complexes higher CNr may occur for Ca at least in glyme-based electrolytes. As stated above, FTIR studies by Bakker et al.[24] suggest that ion pair formation in $A(TFSI)_2$ (A = Mg, Ca, Sr, Ba) electrolytes reaches a maximum around EO:A ratios of 6:1 and with increasing cation size. Judging from the $\nu(SO_2)$ bond vibrations Mg^{2+} was coordinated to the SO_2-oxygens forming a six membered ring with the TFSI anions, while larger cations coordinated in a bidentate fashion to the TFSI-nitrogen and SO_2-oxygen. At lower salt concentrations, ion pairing were not observed and except for PEO:A(TFSI)₂ complexes the maximum conductivity was achieved for EO:A ratios >16:1, except for PEO:Mg(TFSI)₂ that reached its maximum conductivity at a ratio of 9:1. The more recent study by Park et al.,[33] suggested that electrolytes with lower salt contents show slightly higher ionic conductivities.

As previously mentioned, detailed structural data of these complexes are rare, especially for the more recent chloride-free salts. However, information is available for the coordination environments of AX_2 in glyme solutions, which share many similarities with their solid PEO congeners, although in SPEs the salt
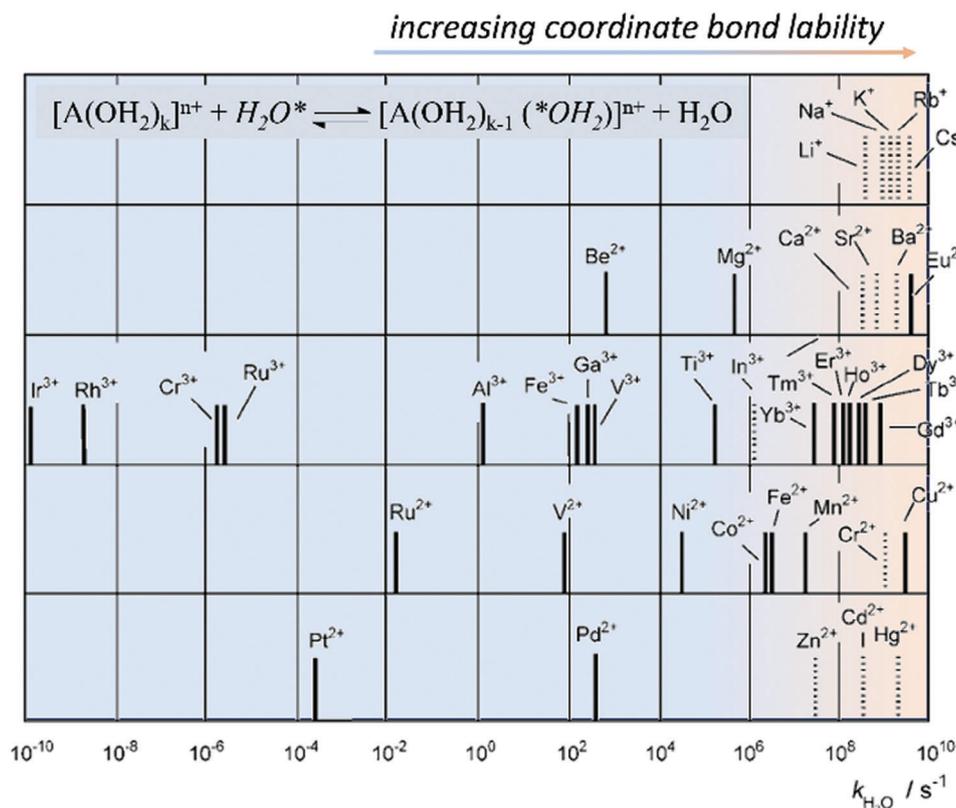
Figure 4. Ligand exchange rates in water for various cations. Adapted with permission.[11] Copyright 2005, Wiley-VCH.

concentration is often more diluted (as previously discussed herein). For the Mg[B(hfip)$_4$]$_2$•3DME complex, Mg is coordinated in a disordered octahedral manner by 3 DME molecules, i.e., fully solvent separated.[92] According to DFT calculations direct coordination between Mg-ions and moieties of the borate-anion are only expected at high salt concentrations.[108] In accordance, Salama et al.[109] showed in structural studies on Mg(TFSI)$_2$ in DME a comparable coordination environment with Mg-ions fully solvated by 3 DME molecules. Using NMR spectroscopy the authors also determined a substantial DME exchange energy of 14 kcal mol^{-1} per ligand, indicating "exceptionally slow exchange rates at RT",[109] which is in agreement with a high overpotential for the Mg stripping process and the associated poor plating/stripping efficiencies.[93] In the Ca[B(hfip)$_4$]$_2$•4DME complex, Ca^{2+} is coordinated by 4 DME molecules in a (distorted) square antiprismatic geometry (CNr = 8), owing to the larger cation size. As a result the O—Ca bond lengths are larger than the corresponding O—Mg bonds (2.43 Å vs 2.06 Å), indicating lower dissociation energies for the dissolution of the Ca-salt.[103] In contrast, for PEO:Ca(OTf) complexes Metha et al.[19] found a stochiometric complex with an EO:Ca ratio of 6:1 with an orthorhombic unit cell. Assuming associated anions contribute to the coordination of the Ca-ion, the CNr is likely between 6 and 9.

2.2. Ion Transport Limitations in Solid Polymer Electrolytes

As already mentioned, breaking of metal–ligand coordination bonds is a prerequisite for cation transport, since cation transport in high-molecular-weight polymers (where the long-range diffusion of chains is negligible) is reliant on the ions moving along or between polymer chains. Irrespective of if the transport takes place in a soft or rigid matrix, such a process can only take place if ligands are exchanged in the cation coordination shell. This makes the cation mobility inherently tied to the ligand exchange rate. **Figure 4** shows the ligand exchange rates in water for a range of mono- and multivalent cations. The residence time of a water molecule in the first coordination shell of Cs$^+$ is ≈200 ps, while in a [Ir(H$_2$O)$_6$]$^{3+}$ complex one water exchange occurs about every 50 years.[110] In the group of alkali metals water exchange rates vary by around one order of magnitude with the Li$^+$-ion at the low end of the series. This is explained by its higher surface charge density, i.e., hard nature (HSAB). Generally, ligands experience little stabilization in complexes with main-group elements, unlike transition metals where the d-orbital occupancy and orbital splitting has a strong impact on the lability and thus the ligand exchange rate.[11] For this reason, alkali and alkaline earth metal ions water exchange rates correlate inversely with cation size. The data clearly shows a notable rate penalty for divalent ions, particularly small and hard ions like Be^{2+} and Mg^{2+}, that should directly translate into a mobility penalty in polymeric systems.

Water might not constitute the most relevant and representative system, as in organic aprotic solvents the formation of contact ion pairs (CIPs) or charged aggregated species is more likely. In fact, molecular dynamics (MD) studies on Li- and Na-salts in propylene carbonate and acetonitrile suggest that the residence times in dilute systems are in the range of a few ps up to tens of ps in concentrated formulations.[111–113] Exchange rates of other
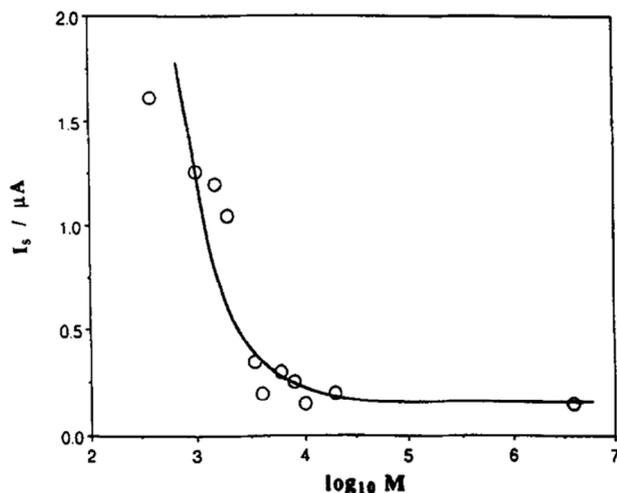
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Figure 5. Steady-state currents (I_s) from dc polarization experiments at 80 °C of PEO-Mg(Tf)$_2$ (EO:Mg, 20:1) polymer electrolytes as a function of molecular weight in symmetrical Hg(Mg)-Hg(Mg) cells. Reproduced with permission.[118] Copyright 1995, Elsevier Ltd.

metal ions in typical organic, aprotic solvent seem to be rare. Borodin et al.[114] found residence times of 1–2 orders higher for Mg(TFSI)$_2$ and Zn(TFSI)$_2$ in Pyr$_{14}$TFSI ionic liquid electrolytes, than with corresponding LiTFSI or NaTFSI salts (low ns range). Recently, Yusupova et al.[115] determined the energy of formation by MD simulation for A^{n+}(ClO$_4$)$_n$ (A = Li, Na, K, Mg, Ca) in sulfolane and found higher CNr's and energies of formation for the alkaline earth metal complexes (exchange rates were not stated). Chen et al. studied Mg-ion transport in a polymeric ionic liquid via MD simulations, which demonstrated that the interaction between Mg^{2+} and FSI$^-$ is too strong and hinders the diffusion of both species. Reducing the metal ion–anion binding strength is thus a key factor in facilitating the conduction of multivalent ions.[116] Although this topic was partially covered for Li-ions for various solvents, in-depth studies (both theoretical and experimental) on ligand exchange rates for multivalent cations in organic, aprotic solvents that could serve as a basis for the design of novel polymer hosts do not seem to exist. It is worth highlighting though that the electrochemical stability of SSIP and CIP complexes play an important role in the passivation mechanisms at the interface of metallic electrodes (Section 2.3), which fostered theoretical works in this area. With appropriate models in place, additional parameters such as the ligand exchange rates might be readily accessible. It is thus reasonable to assume that the order in ligand exchange rates in water should be translatable to other monodentate oxygen donor ligands, bearing in mind that additional chelating and steric effects may be ion size dependent. Since the anion is typically interacting less with the polymeric matrix, a mobility penalty for the cation will translate into a lower cation transference number.

Indeed, as dc polarization measurements on glyme and PEO-based electrolytes with Mg(CF$_3$SO$_3$)$_2$ by Vincent[117] indicated, ion conduction ceases (current drops to zero) as the molecular weight of the polymer increases and the electrolyte is rendered solid (**Figure 5**), whereas corresponding liquid Mg–glyme electrolytes displayed steady-state currents. According to the author,

Mg plating was possible as long as a concerted migration of Mg-ions and the oligomeric solvation sheath was possible. In contrast, the same experiment carried out in a Ca(CF$_3$SO$_3$)$_2$-system (EO:Ca = 20:1), a steady-state current could be obtained even for solid polymer electrolyte compositions.

Following the ligand exchange rate concept discussed above (Figure 4), the water exchange in Mg^{2+} complexes is smaller by three orders of magnitude compared to Ca^{2+}, and thus also appears to correlate to ion mobilities in polyethers.

It is unclear, however, how transferable this concept is to other oxygen-carrying polymers, such as the class of poly-lactones or polycarbonates or entirely different polymeric ligands. Difficulties in reliably measuring transference numbers for other species than Li and possibly also Na have prevented a wide transference number survey of different host materials and cations. This is mainly because the most common method to estimate the transference number, the Bruce–Vincent method, requires non-blocking metal electrodes able to strip/plate at stable potentials.[4,119] While this could be applied to lithium, it is far more complicated for other ions such as Na$^+$,[40] K$^+$,[120] Mg^{2+},[33] and Ca^{2+}. In these cases, the overpotential is often high and the passivation of these metals also affect the polarization results.[28,121] Furthermore, the assumption of full ion dissociation required for these methods is also problematic for multivalent cations as ionic clusters tend to form.[33] Alternative methods, such as the limiting current density method also require symmetric metallic cells to determine the maximum cationic current that the SPE can sustain.[122]

Polarization tests for the metal deposition on metallic substrates (e.g., Cu|Mg), in which the steady-state-to-initial current ratio (i_{ss}/i_0) are of practical use nonetheless, for relative comparisons.[33] There appears to be a fairly direct correlation between the cation–polymer interaction strength and the cation transference number, at least for Li systems.[123] Extrapolating this approach to the divalent Mg^{2+} cation, recent data on cation–polymer interaction strengths indicate that PEO, which is known as an exceptionally good solvent for the similarly-sized Li$^+$, seems to also be exceptionally good at solvating Mg^{2+} (**Figure 6**) compared to other host materials such as PCL and PTMC.[33,124] It remains to be seen whether this is also reflected in the transference numbers for these systems. Although plenty of data appear to identify Mg^{2+} as largely immobile in polymer matrices, that species alone is not the sole charge carrier in magnesium electrolytes. It is likely that an ionic cluster, such as [MgTFSI]$^+$, is more mobile and can carry more than a negligible fraction of the total charge, as recently suggested.[33] In that case, the divalent magnesium ion is practically rendered monovalent. Together with the larger size of this cluster compared to the bare ion, this is likely to have implications for both ligand exchange rates and transference numbers.

Changes in solvent-ion interactions have been monitored by vibrational spectroscopies, i.e., FTIR and Raman spectroscopies (see above), as well as dielectric relaxation spectroscopy[125] and can be helpful in identifying ion-pair formation[126] or studying the polymer dynamics in dependence of the ion-solvent interactions.[37,39,127] In fact, ion coordination and association carry considerably more weight in multivalent systems.
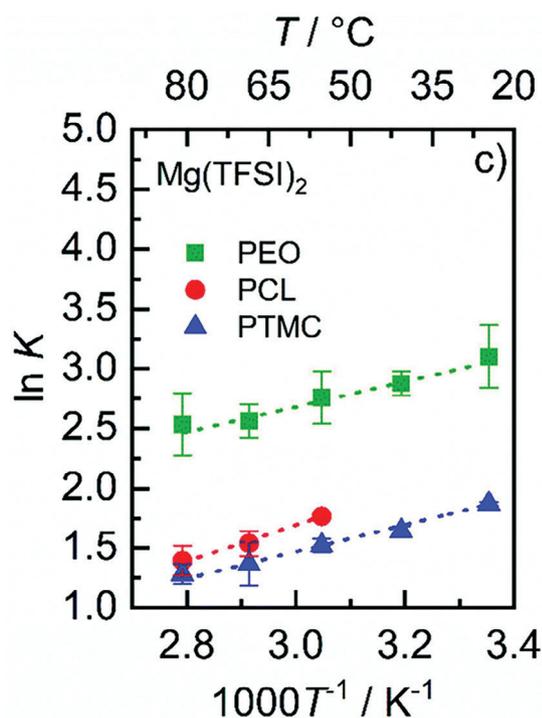
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Figure 6. $\ln K$ versus $1/T$ for the ion binding equilibrium for Mg(TFSI)$_2$-containing polymer electrolytes based on different polymer hosts. Adapted with permission.[124] Copyright 2022, Andersson et al.

For example, the addition of MgCl$_2$ to Mg(TFSI)$_2$/DME electrolytes was found to be highly beneficial in reducing the plating/stripping overpotentials and increasing the Faradaic efficiency of the process.[93] Salama et al.[128] stated that particularly in glymes, cationic clusters such as [MgCl]$^+$, [Mg$_2$Cl$_2$]$^{2+}$, or [Mg$_2$Cl$_3$]$^+$ may form. [MgCl]$^+$ species were also found to contribute to a notable degree to ion transport in PEG:(δ-MgCl$_2$) electrolytes.[38] Chloride-ions in Mg$_x$Cl$_y$ clusters effectively reduce the formal charge of Mg^{2+}, which appears to have a positive influence on the Coulomb interactions of the surrounding coordinating groups, i.e., in reducing solvation energies,[88] and thus facilitate transport and charge transfer properties. It is thus surprising why mixed salt electrolytes have received little attention thus far in SPE application.

Alternative techniques to investigate ion transport are pulsed field gradient or electrophoretic NMR, as they provide information on the self-diffusion coefficient of relevant elements. While these have successfully been used for Li$^+$,[123,129] it is not possible for multivalent cations such as Mg^{2+} and Ca^{2+} due to their low receptivity to NMR experiments (2.68×10^{-4} for ^{25}Mg and 8.68×10^{-6} for ^{43}Ca, compared to 0.27 for ^{7}Li and 0.83 for ^{19}F relative to 1 for ^{1}H). Thus, there are no reports of diffusion for multivalent cations yet in the literature.[28] However, these techniques can provide useful information about the mobility of anions and solvents if they contain other elements, such as ^{19}F and ^{1}H-based.

Overall, investigating the ion transport in multivalent solid polymer electrolytes is not an easy task due to the limitations from the currently used methods. Instead, combining the in-

formation from different techniques will provide more knowledge and understanding of these complicated systems. Although there are some values reported for multivalent cation transference number in literature (and also cited in the text above and Table 2), they should generally be considered with caution.

2.3. Reversibility of Charge-Transfer Processes and Materials Interfaces

One of the main bottlenecks for multivalent batteries is the use of metallic negative electrodes that display high voltage hysteresis due to their dense and poorly cation-conductive interphases between electrode and electrolyte. Unlike for alkali metals, plating and stripping of multivalent ions is a considerable challenge in itself, aside from sufficiently high cation mobility in the electrolyte. The desolvation process of multivalent cations at the interface of negative or positive electrodes is a major rate-limiting factor for the insertion or deposition of cations into inorganic host structures or metallic electrodes, respectively.[130] In the following sections, key strategies to activate Mg or Ca surfaces, to reduce voltage hysteresis and to increase the coulombic efficiency (C.E.) relevant to the development of SPE-based multivalent batteries are discussed. For detailed summaries on the latest developments in the electrode material field, several dedicated recent reviews on the topic are available elsewhere, e.g. ref. [131,132]

2.3.1. Stripping and Plating Processes at Mg and Ca Electrodes

In an early attempt by Vincent[26] to perform stripping/plating experiments from Mg- and Ca-SPEs, the issues to deposit multivalent ions under dc polarization were solved by the use of Mg- and Ca-amalgams (Hg(Mg)/Hg(Ca)) as alternative working and counter electrodes, since attempts to plate directly onto Mg and Ca electrodes were unsuccessful (SPE containing Mg/Ca-triflate-salts in a "methoxy-linked" poly(ethylene oxide; Figure 5). The author also noted a significant overpotential of the stripping process in a 3-electrode setup, in accordance with the finding of Melemad et al.[133] (25 years later).

In regard to the stripping/plating processes, the interphase formation and the A^{2+} mobility across the SEI layer are key factors. In addition, the high reactivity of alkaline earth metals should be considered. Similarly, to the increasing reactivities along the group of alkali metals, i.e., Li < Na < K < ..., Ca is more reactive than Mg. This might not be directly obvious, as both metals can be handled under air and moisture as they form a passivating oxide layer, but exposed Mg or Ca metal surfaces (e.g., by electrodeposition) are highly reactive towards electrolyte components.

Electrolyte Stability: Particularly relevant in this context are the cathodic stabilities of the boron-based and TFSI anions that have received much attention. For example, it was found that Ca deposition in electrolytes comprising Ca(BF$_4$)$_2$ and Ca(ClO$_4$)$_2$, occurred at elevated temperatures above 50 °C,[10] whereas reversible stripping/plating in liquid electrolytes containing Ca(TFSI)$_2$ was not possible. On a broader scope, this observation has to be understood from two angles: 1) the electronic structures of constituents (anion or solvent) in the solvation sphere changes when coordinating to hard, Lewis-acidic

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multivalent cations and 2) the high reactivities of the alkaline earth metals.

The choice of solvent determines whether solvent-separated ion pairs (SSIPs), CIPs or aggregates are formed with the electrolyte salt. DFT calculations showed that the cathodic stability of uncoordinated TFSI (SSIP) is higher than in CIP configurations where anion(s) are coordinated to Mg^{2+} via its oxygen or nitrogen atoms.[134] The species in the solvation shell that the cation carries with it to the electrode surface are thus prone to facilitated degradation processes.[135] As a result, solvents that cause CIP formation show no or very inefficient (low C.E.) Mg-deposition and significant anion degradation, while in SSIP the TFSI decomposition is minor. For example, when Mohtadi et al.[99] introduced $Mg(BH_4)_2$ salts as halide-free electrolyte salts with promising plating/stripping characteristics the C.E. efficiency was found to be higher in solvents with higher degrees of ion dissociation. Chelating glyme solvents[99,100] proofed to be more effective than ether solvents (e.g., THF or diethyl ether) that generated the μ-hydride-bridged $[Mg(\mu\text{-}H)_2BH_2]_2$ CIP that dissociate poorly in ether solvents like THF or diethyl ether. In contrast, high donor number solvents, such as DMF and chelating glyme solvents (e.g., di- or tetraglyme) were found more effective in separating CIPs[91] and thus allow for more effective Mg-deposition. Similar effects likely played a role in PEG:(δ-MgX_2) electrolytes (X = Cl,[35] I[136]), where PEG contributes to the formation of solvent-separated Mg^{2+} and $[MgX]^+$ species that facilitate the Mg deposition process.[39]

Furthermore, the instability of $[Mg(TFSI)]^+$- and $[Mg(PF_6)]^+$-CIPs was confirmed also by ab initio molecular dynamic simulations (AIMD).[135,137] In the aforementioned polarization experiment by Park et al.[33] of Mg^{2+} from a PTMC-PCL SPE on Cu found mainly TFSI decomposition products and concluded that the measured current originated predominantly from degradation of labile CIP, e.g. $[MgTFSI]^+$. The resulting fluoride-containing surface layers on the Mg-anode has an inhibiting effect on the electrode process. Similar issues have been encountered in liquid electrolytes with $Ca(TFSI)_2$.[10] In cases where anions exhibit intrinsically higher cathodic stability, as in many boron-based anions (e.g., BH_4^-, BF_4^- or $[B(hfip)_4]^-$), plating and stripping (liquid electrolytes) can take place despite CIP formation, though with smaller C.E. than in other solvent/salt compositions.[103,108,138] Interestingly, for corresponding $Mg[B(hfip)_4]_2$-electrolyte plating/stripping experiments C.E.>98% were found over the first 100 cycles.[92] For comparison, in ionic liquid systems comprising ([EmImCl/(AlCl$_3$)$_{1.5}$](δ-$MgCl_2$)$_x$)[139] or ([Pyr$_{14}$Cl/(AlCl$_3$)$_{1.5}$](δ-$MgCl_2$)$_x$)[127] or in Gignard-based electrolytes[88] plating/stripping efficiencies beyond >99.5% could be achieved. However, Cl-ions appear to take a special role in both the ion solvation and deposition/dissolution mechanisms at the metallic negative electrodes. For instance, $Mg(TFSI)_2$/DME mixtures exhibit high cation-solvent interactions rendering the complex particularly stable during charge-transfer reactions.[109] As a result, desolvation, as one of the necessary steps to plate Mg-ions, comes at a high energy penalty. Upon addition of $MgCl_2$ the resulting $[MgCl]^+$ (or higher order) clusters facilitate the charge-transfer by weakening the ion-solvent interactions.[128] Moreover, in their role as surface-adsorbent anions they also appear to suppress $TFSI^-$ degradation at the electrode interface.[88,128] Hence, the above discussed solvent donor numbers and the degree of ion association as a function of salt concentrations play a more important role than in alkali metal cell chemistries. These recent findings are important factors to consider in future electrolyte SPE design, as TFSI salts are the most commonly used electrolyte salts for SPE applications.
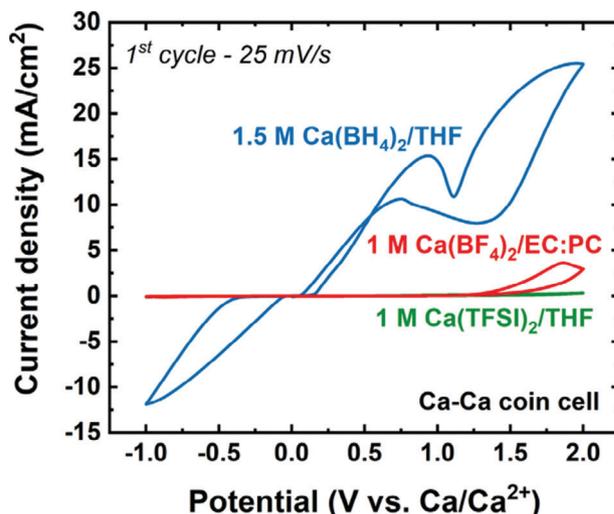

Figure 7. 1st cycle CV of Ca plating and stripping in three different electrolyte formulations in a Ca-Ca symmetrical cell. Reproduced with permission.[133] Copyright 2020, Melemed et al.

SEI Layers and Surface Activation: A recent X-ray photoelectron spectroscopy (XPS) study by Ponrouch and coworkers[76] found substantial differences between the passivation layer compositions formed on Ca-metal electrodes in dependence of the anion (TFSI and BF_4, respectively). In carbonate-based $Ca(TFSI)_2$ electrolytes, $CaCO_3$ formation appears to be a particular problem, while in the presence of BF_4^-, higher contents of CaF_2 and organoborate species were found as primary components in the passivation layer. The calculated A^{2+} migration energy barriers indicate that most inorganic SEI compounds that are formed from either salt or solvent degradation, particularly ACO_3, AO, and AF_2 (A = Mg, Ca), pose high kinetic barriers that prevent electrodeposition even at very low rates.[76] The interphase formation thus seems to play an even more important role than for Li-ion batteries, considering that activation and passivation of metallic electrodes only work with a limited selection of electrolyte salts. One exception with comparatively high A^{2+} mobility is CaH_2, which can be formed on the Ca-surface with $Ca(BH_4)_2$ in THF as electrolyte and that enables room temperature plating and stripping.[75]

According to Melemed et al., most stripping/plating experiments are still conducted on other metallic substrates as working electrodes, like Au, Pt or Cu, in asymmetric cell configurations against a Ca counter electrode[133]. As the authors outline in their study, the preparation of the Ca-electrode and even the direction of current on the first CV scan matters greatly with respect to the observed voltammetric features in CV experiments (**Figure 7**). However, at least in the aforementioned THF:$Ca(BH_4)_2$ electrolyte, the processing history of Ca-foil electrodes disappears on following cycles, which can be understood as an effective electropolishing step that resets the interface and activates the
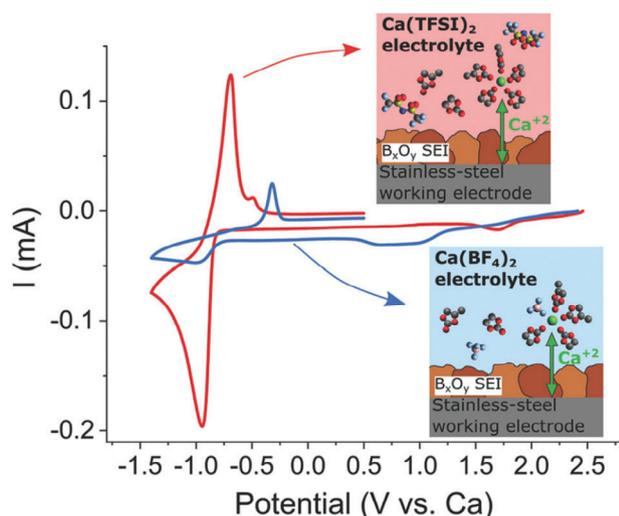
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Figure 8. Passivation strategy on stainless steel electrodes. Adapted with permission.[76] Copyright 2020, Forero-Saboya et al.

surface. This ties in with their conclusion that once Ca surface deposits have been formed, stripping/plating on following cycles is facilitated.

Surface Coatings: Forero-Saboya et al.[76] demonstrated that passivated stainless steel electrodes can be prepared by a pre-passivation step in a $Ca(BF_4)_2$ electrolyte (**Figure 8**).

After this surface treatment, electrolytes based on both BF_4^- and TFSI could be cycled reversibly. Other approaches aimed to form interphases on Mg or Ca substrates with higher cation mobility and protective functionality to reduce the degree of electrolyte degradation. For example, pretreatments of Mg foil with various chlorides of group IV and V elements in DME, such as $BiCl_3$-DME[140], $SnCl_2$-DME[141], $SbCl_3$-DME[142], or $GeCl_4$-DME[143] solutions. The treatment produces an interphase comprising Mg_xM_y (M = Bi, Sn, Sb, Ge) alloys and $MgCl_2$. The coatings decreased the voltage hysteresis and greatly prolonged cycling in Mg/Mg symmetrical cells.

Novel electrode materials. With the rising interest in multivalent battery systems, new negative electrodes are being developed that could potentially circumvent some of the bottlenecks associated with Mg and Ca metal electrodes. Alloying, as described for the surface coatings above, can remove surface oxides and hydroxides that are considered a significant hindrance for ion diffusion. In addition, the SEI components formed at the electrode-electrolyte interface can inhibit charge-transfer entirely as a result of the reactive metallic electrodes. Alloys could potentially bypass passivation issues, such as Ca-Si[144] and Ca-Sn[145] alloys. The latter demonstrated that cycling between the $CaSn_3$ composition and β-Sn, was possible with significantly reduced capacity loss and lower voltage hysteresis at room temperature in a DME:Ca[B(hfip)$_4$]$_2$ liquid electrolyte.

2.3.2. Cell Tests with Positive Electrodes

In order to demonstrate ion transport, building symmetrical cells and cell configurations with positive electrode materials appears to be particularly relevant when traditional means

fail to investigate ion transport (Section 2.2). Storing multivalent ions comes with additional challenges with respect to solid-state diffusion (e.g., stronger electrostatic interactions with host lattice) and charge-transfer kinetics (e.g., host might require several redox centers and high desolvation energy slow down the kinetics). Some materials thus require elevated temperatures to achieve the required cation mobility in the material to access full capacity. Hence, SPEs that typically operate at higher temperatures anyway might represent an attractive materials class for those applications, as liquid electrolytes often show increased degrees of degradation under such conditions.

An early work by Patrick et al.[146] examined a selection of positive electrodes, including TiS_2 and V_6O_{13}, in Mg/PEO:MgX$_2$/cathode configurations (PEO M_n = 4 × 10^{-6} g mol^{-1}; X = SCN$^-$, ClO$_4^-$). All configurations showed cell voltages between 1.7 V (TiS_2) and 2.0 V (V_6O_{13}) and passing current over an extended time interval (up to 3000 h at 1 μA) was possible at temperatures down to 15 °C. However, cycling experiments were not conducted (also, SPEs contained residual water due to the drying procedure).

Transition metal Dichalcogenes: Especially, TiS_2 is well known as positive electrode materials of the first hour.[147,148] TiS_2, but also V_6O_{13} have been studied for solid-state, SPE-based Li batteries (at temperatures of up to 100 °C).[149] In a recent example Shao et al.[52] cycled a Mg/PEO:(Mg(BH$_4$)$_2$-MgO)/Mo$_6$S$_8$ cell within the voltage limits of 0.8–1.35 V and a capacity of ≈80–90 mAh g^{-1} over 100 cycles with high C.E. on the long term, but a high initial irreversible loss of more than 50% (the solid-state cell operated at 100°C). In fact, the Chevrel phase Mo_6S_8 is a prominent material as a result of high solid-state Mg^{2+}-mobility.[150,151]

Prussian Blue Analogues (PBAs): Another increasingly relevant material class, particularly for demonstrator cells on lab scale, are the Prussian blue analogues (PBA), with the general structure $A_xM'[M''(CN)_6]$ where A is in this case an alkali or alkaline earth metal and M'/M'' are typically transition metals, especially Fe. PBAs are exceptionally flexible when it comes to insertion of mono-[152] or multivalent ions[153] of various ionic radii, e.g. $ACu[Fe(CN)_6]$ (e.g., A = Zn^{2+}, Ni^{2+}, La^{3+}, Al^{3+}, etc.) reached capacities of 40–60 mAh g^{-1} and electrode potentials between 0.6–1.2 V versus SHE[153]. For the reversible Mg^{2+} or Ca^{2+} insertion in non-aqueous electrolytes, PBA compositions such as M'/M'' = Fe/Fe[154], Ni/Fe[155], or Mn/Fe[156] have been studied. PBAs are well-suited for cell tests of SPE-based solid state cells, as shown for instance recently for Na-[157,158] and K-ion[120,159] cells.

Organic electrodes – the all-round solution? For multivalent systems organic electrodes, based on redox-active molecules or polymers, offer an interesting way to test novel electrolytes and electrolyte salts and bypass the interface chemistry issues encountered with metallic electrodes. In fact, redox active organic compounds are not bound to a certain cell chemistry and are thus attractive electrode materials for emerging battery technologies. According to Bitenc et al.[160] lower average voltage in systems with redox-active organic molecules could be compensated in the future by new materials with higher capacities than inorganic materials could deliver. Furthermore, they pave the way toward all-polymer, flexible batteries. 1,4-Polyantraquinone[161] is one example that has been employed recently by Zhao-Karger et al.[145] as an organic counter electrode to test the

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cyclability of Ca-battery negative electrodes. Moreover, there is plenty of room in the chemical space to tailor organic electrodes to the specific requirements of the desired electrochemical system.[145,160–165]

3. Summary and Outlook

The search for alternative high-energy battery technologies to lithium-ion batteries has fostered increasing activities on multivalent battery systems. Prominent examples are Mg-, Ca-, and Al-based batteries. Two of the biggest challenges in these three systems is ion transport in the bulk electrolyte and the electrode–electrolyte interactions at the electrode interface. In the search for better electrolytes, multivalent cation transport has been revisited, particularly for Mg-ion batteries. Previous studies concluded that Mg^{2+} is only mobile as long as the polymer is able to move with the ion (oligoether solvents), and ion motion was found to cease as the molecular weight increased. It is thus encouraging to look toward the latest improvements in the field to highlight that Mg^{2+} mobility can be achieved. However, it is important to ensure that ionic conductivities originate from cation motion and not solely by the anions.

The challenge to move multivalent cations with high charge density in a polymer matrix of chelating and strongly coordinating functional groups is and continues to be a limiting factor for ion transport even for monovalent cations. Here, novel and interesting strategies to improve ion transport may arise from studying multivalent electrolytes and battery systems in general.

With respect to a larger variety of currently investigated cations and possibly novel systems to come, there is likely a need to tailor the polymer properties, in particular toward their coordinating properties. As pointed out, strong coordination, i.e., strong polymer–cation interactions, will lead to good ion separation but restricted cation mobility, whereas weaker coordination results in ion pairing and cluster formation but higher cation mobility, though for a smaller fraction of cations.[123] This is particularly relevant for multivalent systems, where significant anion degradation and low degrees of cation deposition was found in cases of ion pair formation.[137] The TFSI anion appears to be particularly prone to this process. Interestingly, bulky and non-coordinating anions, such as the tetrakis-(hexafluoroisopropyloxy)borate ($[B(hfip)_4]^-$) anion, show better cathodic stability and considerable improvements[104] over previous electrolyte salt generations, rendering them attractive new salts to be studied in polymer electrolytes.

In addition, investigations have mostly studied PEO as the dominant polymer host in the field and thus a natural starting point for SPE studies. For Mg-SPEs addition of inorganic fillers to form PEO-salt-filler composites showed promising results. Many studies on alternative polymer hosts have so far focused on PVA- and poly(carbonate)-based SPEs. For larger cations like Ca^{2+} extending the polyether O-to-O distance (e.g., PTHF) was also considered. Prospectively, moving away from oxygen coordinating groups entirely might become more relevant in multivalent systems in the context of optimizing the coordination environment. There are still a number of interesting polymer classes that have been studied for Li-systems but so far have been rarely considered for SPEs of multivalent systems, such as poly(dimethyl siloxane)[39] or poly(ethylene imine).[3] In addition, different poly-

mer properties can be combined in complex copolymeric structures, which can be a continuous source for novel innovative materials.

Such efforts can be assisted by ranking and assessing different coordinating groups using concepts like the ligand exchange rates.[124] The concept could be further expanded, as it represents a possible descriptor to ion mobility in polymers as a basis for theoretical studies.[166,167] Cations with higher surface charge interact stronger with polymer coordinating groups and thus could theoretically favor different transport pathways. In this context, it is worth highlighting that more work remains to be done to understand polymer dynamics and transport mechanisms of multivalent cations in polymer matrices. This applies in particular to materials other than PEO.

Because of the variety of different polymer structures, the use of the $EO:A^{n+}$ ratio that is traditionally used for PEO-based SPEs is less useful. In literature, salt contents are also provided in mol.% and wt.%. While each of these parameters has its justification, it is important to finding common conventions, e.g., by stating weight ratios (wt.%) in every experimental section in addition to other possible proportions. Similarly, comparing ionic conductivities between different studies can be challenging if values for different temperatures are reported. Room temperature is not clearly defined and ionic conductivities for elevated temperatures vary in the range from 40–90 °C. A set of consistently reported ionic conductivities could consist for instance of values measured at 25, 45, and 65 °C (and possibly 85 °C), i.e., ambient, near-ambient and above the PEO melting temperature. As a main key performance indicator for SPEs, common conventions for ionic conductivities and salt contents would allow theorists to more conveniently compare simulated and experimental data.

Major *bottlenecks* are also encountered with respect to quantifying cation transport or determination of characteristic physical properties such as the transport or transference number. Established techniques, particularly transport number measurements via cell polarization and NMR spectroscopy, and even the commonly used electrochemical impedance spectroscopy (EIS) are of limited use, at least for Mg- and Ca-systems. The limitations in regard to polarization experiments are rooted in the high interfacial resistances of metallic Mg or Ca electrodes and the formation of passivation layers with poor cation transport properties. This highlights the need for reliable and convenient methods to measure transference numbers in these systems, which currently do not exist.

This issue extends to experiments on a cell level to demonstrate through cycling experiments ion transport and reversibility. As it turns out, unlike alkaline monovalent ion-conductors, development of electrolytes for multivalent systems requires clear strategies to manage the electrode surface chemistry. More promising than metallic electrodes could be the use of alloys, either as electrode material or as surface coatings, which facilitate ion transport across the electrode–electrolyte interface. Ca-Sn-alloys[131] for example represent a promising alternative to calcium amalgam that was used in the past.[117] Another alternative to metal electrodes are organic electrodes that could also be used to investigate SPEs in multivalent systems.

Overall, in order to overcome the current challenges with multivalent solid polymer electrolytes, the research field should focus on new polymer hosts and salt anions to increase the cation

transport and polymer chain dynamics. More electrochemically stable systems to avoid parasitic electrolyte degradation on reactive electrode interfaces and decrease sources of high resistance in the cell setup. Finally, SPEs need to be put to application tests at cell level with relevant electrode active materials, to not only investigate the SPE's properties in more realistic environments but also to ultimately foster the development toward better functioning battery cells.

Conflict of Interest

The authors declare no conflict of interest.

[1] M. Armand, *Solid State Ionics* **1983**, *9–10*, 745.
[2] A. Mauger, C. M. Julien, J. B. Goodenough, K. Zaghib, *J. Electrochem. Soc.* **2020**, *167*, 070507.
[3] J. R. Nair, L. Imholt, G. Brunklaus, M. Winter, *Electrochem. Soc. Interface* **2019**, *28*, 55.
[4] P. Bruce, F. Krok, C. Vincent, *Solid State Ionics* **1988**, *27*, 81.
[5] Å. Wendsjö, J. Lindgren, J. O. Thomas, G. C. Farrington, *Solid State Ionics* **1992**, *53–56*, 1077.
[6] P. Bruce, J. Nowinski, F. Gray, C. Vincent, *Solid State Ionics* **1990**, *38*, 231.
[7] F. M. Gray, *Polymer Electrolytes*, Royal Society Of Chemistry, United Kingdom **1997**.
[8] H. Zhang, L. Qiao, H. Kühnle, E. Figgemeier, M. Armand, G. G. Eshetu, *Energy Environ. Sci.* **2023**, *16*, 11.
[9] A. M. Melemed, A. Khurram, B. M. Gallant, *Batteries Supercaps* **2020**, *3*, 570.
[10] A. Ponrouch, C. Frontera, F. Bardé, M. R. Palacín, *Nat. Mater.* **2016**, *15*, 169.
[11] S. F. Lincoln, *Helv. Chim. Acta* **2005**, *88*, 523.
[12] L. L. Yang, A. R. Mcghie, G. C. Farrington, *J. Electrochem. Soc.* **1986**, *133*, 1380.
[13] L. Yang, R. Huq, G. Farrington, G. Chiodelli, *Solid State Ionics* **1986**, *18–19*, 291.
[14] R. Huq, *Solid State Ionics* **1988**, *28–30*, 990.
[15] J. J. Fontanella, M. C. Wintersgill, J. P. Calame, C. G. Andeen, *J. Polym. Sci. Polym. Phys.* **1985**, *23*, 113.
[16] V. Di Noto, M. Bettinelli, M. Furlani, S. Lavina, M. Vidali, *Macromol. Chem. Phys.* **1996**, *197*, 375.
[17] V. Di Noto, M. Furlani, S. Lavina, *Polym. Adv. Technol.* **1996**, *7*, 759.
[18] A. Patrick, M. Glasse, R. Latham, R. Linford, *Solid State Ionics* **1986**, *18–19*, 1063.
[19] M. A. Mehta, P. Lightfoot, P. G. Bruce, *Chem. Mater.* **1993**, *5*, 1338.
[20] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724.
[21] V. Di Noto, M. Fauri, Magnesium-Based Primary (Non-Rechargeable) and Secondary (Rechargeable) Batteries, WO 01/09972 A1, **2001**.
[22] R. G. Pearson, *J. Chem. Edu.* **1968**, *45*, 581.
[23] J. Thomson, P. Lightfoot, P. G. Bruce, *Solid State Ionics* **1996**, *85*, 203.
[24] A. Bakker, S. Gejji, J. Lindgren, K. Hermansson, M. M. Probst, *Polymer (Guildf)* **1995**, *36*, 4371.
[25] R. Huq, G. C. Farrington, *Solid State Ionics* **1988**, *28–30*, 990.
[26] R. Huq, G. C. Farrington, *J. Electrochem. Soc.* **1988**, *135*, 524.
[27] J. Mindemark, M. J. Lacey, T. Bowden, D. Brandell, *Prog. Polym. Sci.* **2018**, *81*, 114.
[28] B. Park, J. L. Schaefer, *J. Electrochem. Soc.* **2020**, *167*, 070545.
[29] M. Jaipal Reddy, P. P. Chu, *J. Power Sources* **2002**, *109*, 340.
[30] S. Ramalingaiah, D. S. Reddy, M. J. Reddy, E. Laxminarsaiah, U. V. S. Rao, *Mater. Lett.* **1996**, *29*, 285.
[31] M. Jaipal Reddy, P. P. Chu, *Solid State Ionics* **2002**, *149*, 115.
[32] N. S. Vrandecic, M. Erceg, M. Jakic, I. Klaric, *Thermochim. Acta* **2010**, *498*, 71.
[33] B. Park, R. Andersson, S. G. Pate, J. Liu, C. P. O'brien, G. Hernández, J. Mindemark, J. L. Schaefer, *Energy Mater. Adv.* **2021**, *2021*, 9895403.
[34] P. Walke, J. Venturini, R. J. Spranger, L. Van Wüllen, T. Nilges, *Batteries Supercaps* **2022**, *5*, 202200285.
[35] V. D. Noto, S. Lavina, D. Longo, M. Vidali, *Electrochim. Acta* **1998**, *43*, 1225.
[36] M. Vittadello, P. E. Stallworth, F. M. Alamgir, S. Suarez, S. Abbrent, C. M. Drain, V. Di Noto, S. G. Greenbaum, *Inorganica Chim. Acta* **2006**, *359*, 2513.
[37] M. Piccolo, G. A. Giffin, K. Vezzù, F. Bertasi, P. Alotto, M. Guarnieri, V. Di Noto, *ChemSusChem* **2013**, *6*, 2157.
[38] V. Di Noto, *Solid State Ionics* **2002**, *147*, 309.
[39] V. Di Noto, *J. Phys. Chem. B* **2002**, *106*, 11139.
[40] J. Serra Moreno, M. Armand, M. B. Berman, S. G. Greenbaum, B. Scrosati, S. Panero, *J. Power Sources* **2014**, *248*, 695.
[41] A. D. Khudyshkina, U.-C. Rauska, A. J. Butzelaar, M. Hoffmann, M. Wilhelm, P. Theato, F. Jeschull, *Batteries Supercaps* **2023**, 202300404.
[42] J. Feng, L. Wang, Y. Chen, P. Wang, H. Zhang, X. He, *Nano Convergence* **2021**, *2021*, 2.
[43] F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M. A. Hendrickson, *Electrochim. Acta* **2001**, *46*, 2457.
[44] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* **1998**, *394*, 456.
[45] C. C. Tambelli, A. C. Bloise, A. V. Rosário, E. C. Pereira, C. J. Magon, J. P. Donoso, *Electrochim. Acta* **2002**, *47*, 1677.
[46] J. L. Keddie, R. A. L. Jones, R. A. Cory, *Faraday Discuss.* **1994**, *98*, 219.
[47] P. Rittigstein, R. D. Priestley, L. J. Broadbelt, J. M. Torkelson, *Nat. Mater.* **2007**, *6*, 278.
[48] N. Boaretto, L. Meabe, M. Martinez-Ibañez, M. Armand, H. Zhang, *J. Electrochem. Soc.* **2020**, *167*, 070524.
[49] B.-K. Choi, K.-H. Shin, *Solid State Ionics* **1996**, *86–88*, 303.
[50] M. A. K. L. Dissanayake, L. R. A. K. Bandara, L. H. Karaliyadda, P. A. R. D. Jayathilaka, R. S. P. Bokalawala, *Solid State Ionics* **2006**, *177*, 343.
[51] K. Perera, M. A. K. L. Dissanayake, P. W. S. K. Bandaranayake, *Mater. Res. Bull.* **2004**, *39*, 1745.

[52] Y. Shao, N. N. Rajput, J. Hu, M. Hu, T. Liu, Z. Wei, M. Gu, X. Deng, S. Xu, K. S. Han, J. Wang, Z. Nie, G. Li, K. R. Zavadil, J. Xiao, C. Wang, W. A. Henderson, J.-G. Zhang, Y. Wang, K. T. Mueller, K. Persson, J. Liu, *Nano Energy* **2015**, *12*, 750.

[53] R. C. Agrawal, D. K. Sahu, Y. K. Mahipal, R. Ashrafi, *Mater. Chem. Phys.* **2013**, *139*, 410.

[54] R. K. Tubbs, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 4181.

[55] N. Voigt, L. Van Wüllen, *Solid State Ionics* **2012**, *08*, 8.

[56] G. Ek, F. Jeschull, T. Bowden, D. Brandell, *Electrochim. Acta* **2017**, *246*, 208.

[57] R. Manjuladevi, S. Selvasekarapandian, M. Thamilselvan, R. Mangalam, S. Monisha, P. C. Selvin, *Ionics (Kiel)* **2018**, *24*, 3493.

[58] R. Manjuladevi, M. Thamilselvan, S. Selvasekarapandian, R. Mangalam, M. Premalatha, S. Monisha, *Solid State Ionics* **2017**, *308*, 90.

[59] R. Manjuladevi, M. Thamilselvan, S. Selvasekarapandian, P. Christopher Selvin, R. Mangalam, S. Monisha, *Ionics (Kiel)* **2018**, *24*, 1083.

[60] F. Jeschull, L. Zhang, L. Kondracki, F. Scott, S. Trabesinger, *J. Phys. Energy* **2023**, *5*, 025003.

[61] S. Kiruthika, M. Malathi, S. Selvasekarapandian, K. Tamilarasan, T. Maheshwari, *Polym. Bull.* **2020**, *77*, 6299.

[62] A. Ab Aziz, Y. Tominaga, *Ionics (Kiel)* **2018**, *24*, 3475.

[63] A. R. Polu, R. Kumar, *Bull. Mater. Sci.* **2014**, *37*, 309.

[64] A. R. Polu, R. Kumar, K. V. Kumar, N. K. Jyothi, *AIP Conf. Proc.* **2013**, *1512*, 996.

[65] M. Sundar, S. Selladurai, *Ionics (Kiel)* **2006**, *12*, 281.

[66] D. A. Sundermann, B. Park, V. Hirschberg, J. L. Schaefer, P. Théato, *ACS Omega* **2023**, *8*, 23510.

[67] S. Kiruthika, M. Malathi, S. Selvasekarapandian, K. Tamilarasan, V. Moniha, R. Manjuladevi, *J. Solid State Electrochem.* **2019**, *23*, 2181.

[68] M. Mahalakshmi, S. Selvanayagam, S. Selvasekarapandian, M. V. L. Chandra, P. Sangeetha, R. Manjuladevi, *Ionics (Kiel)* **2020**, *26*, 4553.

[69] M. Sadiq, M. M. H. Raza, M. Zulfequar, M. Ali, J. Ali, in *Advanced Functional Materials and Devices* (Eds: S. B. Krupanidhi, V. Gupta, A. Sharma Kaushik, A. K. Singh), Springer, Singapore **2022**, p. 17.

[70] J. Koliyoor, Ismayil, S. Hegde, R. Vasachar, G. Sanjeev, *J. Appl. Polym. Sci.* **2022**, *139*, 51826.

[71] S. B. Aziz, S. Al-Zangana, H. J. Woo, M. F. Z. Kadir, O. G. h. Abdullah, *Results Phys* **2018**, *11*, 826.

[72] R. D. Alves, L. C. Rodrigues, J. R. Andrade, A. Pawlicka, L. Pereira, R. Martins, E. Fortunato, M. M. Silva, *Mol. Cryst. Liq. Cryst.* **2013**, *570*, 1.

[73] T. P., A. Ramalingam, S. Selvasekarapandian, S. R. Srikumar, R. Manjuladevi, *Ionics (Kiel)* **2020**, *26*, 789.

[74] T. Ponraj, A. Ramalingam, S. Selvasekarapandian, S. R. Srikumar, R. Manjuladevi, *Polym. Bull.* **2021**, *78*, 35.

[75] D. Wang, X. Gao, Y. Chen, L. Jin, C. Kuss, P. G. Bruce, *Nat. Mater.* **2018**, *17*, 16.

[76] J. Forero-Saboya, C. Davoisne, R. Dedryvère, I. Yousef, P. Canepa, A. Ponrouch, *Energy Environ. Sci.* **2020**, *13*, 3423.

[77] C. S. Martinez-Cisneros, A. Fernandez, C. Antonelli, B. Levenfeld, A. Varez, K. Vezzù, V. Di Noto, J.-Y. Sanchez, *Electrochim. Acta* **2020**, *353*, 136525.

[78] Y. Hu, F. Zeng, Q. Wan, J. Yin, J. Liu, *J. Phys. Chem. C* **2017**, *121*, 16629.

[79] F. S. Genier, C. V. Burdin, S. Biria, I. D. Hosein, *J. Power Sources* **2019**, *414*, 302.

[80] N. S. Mohd Rafi, S. Z. Z. Abidin, S. R. Majid, R. Zakaria, *Int. J. Electrochem. Sci.* **2022**, *17*, 220713.

[81] D. Vanitha, S. A. Bahadur, N. Nallamuthu, A. Shunmuganarayanan, A. Manikandan, *J. Nanosci. Nanotechnol.* **2018**, *18*, 1723.

[82] J. Wang, F. S. Genier, H. Li, S. Biria, I. D. Hosein, *ACS Appl. Polym. Mater.* **2019**, *1*, 1837.

[83] H. Ford, C. Cui, J. Schaefer, *Batteries* **2020**, *6*, 11.

[84] S. Pathreeker, I. D. Hosein, *ACS Appl. Polym. Mater.* **2022**, *4*, 6803.

[85] S. Biria, S. Pathreeker, F. S. Genier, I. D. Hosein, *ACS Appl. Polym. Mater.* **2020**, *2*, 2111.

[86] S. Biria, S. Pathreeker, F. S. Genier, F.-H. Chen, H. Li, C. V. Burdin, I. D. Hosein, *ACS Omega* **2021**, *6*, 17095.

[87] F. Baskoro, H. Q. Wong, H.-J. Yen, *ACS Appl. Energy Mater.* **2019**, *2*, 3937.

[88] R. Attias, M. Salama, B. Hirsch, Y. Goffer, D. Aurbach, *Joule* **2019**, *3*, 27.

[89] N. Pour, Y. Gofer, D. T. Major, D. Aurbach, *J. Am. Chem. Soc.* **2011**, *133*, 6270.

[90] R. E. Doe, R. Han, J. Hwang, A. J. Gmitter, I. Shterenberg, H. D. Yoo, N. Pour, D. Aurbach, *Chem. Commun.* **2014**, *50*, 243.

[91] J. D. Forero-Saboya, E. Marchante, R. B. Araujo, D. Monti, P. Johansson, A. Ponrouch, *J. Phys. Chem. C* **2019**, *123*, 29524.

[92] Z. Zhao-Karger, M. E. Gil Bardaji, O. Fuhr, M. Fichtner, *J. Mater. Chem. A* **2017**, *5*, 10815.

[93] I. Shterenberg, M. Salama, H. D. Yoo, Y. Gofer, J.-B. Park, Y.-K. Sun, D. Aurbach, *J. Electrochem. Soc.* **2015**, *162*, A7118.

[94] C. Wall, Z. Zhao-Karger, M. Fichtner, *ECS Electrochem. Lett.* **2015**, *4*, C8.

[95] S. Yagi, A. Tanaka, Y. Ichikawa, T. Ichitsubo, E. Matsubara, *J. Electrochem. Soc.* **2013**, *160*, C83.

[96] D. Lv, T. Xu, P. Saha, M. K. Datta, M. L. Gordin, A. Manivannan, P. N. Kumta, D. Wang, *J. Electrochem. Soc.* **2013**, *160*, A351.

[97] D. Aurbach, R. Skaletsky, Y. Gofer, *J. Electrochem. Soc.* **1991**, *138*, 3536.

[98] P. G. Bruce, C. A. Vincent, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 3187.

[99] R. Mohtadi, M. Matsui, T. S. Arthur, S.-J. Hwang, *Angew. Chem., Int. Ed.* **2012**, *51*, 9780.

[100] Z. Ma, M. Kar, C. Xiao, M. Forsyth, D. R. Macfarlane, *Electrochem. Commun.* **2017**, *78*, 29.

[101] K. Ta, R. Zhang, M. Shin, R. T. Rooney, E. K. Neumann, A. A. Gewirth, *ACS Appl. Mater. Interfaces* **2019**, *11*, 21536.

[102] A. E. Shirk, D. F. Shriver, *J. Am. Chem. Soc.* **1973**, *95*, 5901.

[103] Z. Li, O. Fuhr, M. Fichtner, Z. Zhao-Karger, *Energy Environ. Sci.* **2019**, *12*, 3496.

[104] A. Shyamsunder, L. E. Blanc, A. Assoud, L. F. Nazar, *ACS Energy Lett.* **2019**, *4*, 2271.

[105] J. Luo, Y. Bi, L. Zhang, X. Zhang, T. L. Liu, *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 6967.

[106] B. S. Parimalam, B. L. Lucht, *J. Electrochem. Soc.* **2018**, *165*, A251.

[107] M. Elmanzalawy, E. Sanchez-Ahijón, O. Kisacik, J. Carretero-González, E. Castillo-Martínez, *ACS Appl. Energy Mater.* **2022**, *5*, 9009.

[108] P. Jankowski, Z. Li, Z. Zhao-Karger, T. Diemant, M. Fichtner, T. Vegge, J. M. G. Lastra, *Energy Storage Mater.* **2022**, *45*, 1133.

[109] M. Salama, I. Shterenberg, H. Gizbar, N. N. Eliaz, M. Kosa, K. Keinan-Adamsky, M. Afri, L. J. W. Shimon, H. E. Gottlieb, D. T. Major, Y. Gofer, D. Aurbach, *J. Phys. Chem. C* **2016**, *120*, 19586.

[110] L. Helm, A. E. Merbach, *Coord. Chem. Rev.* **1999**, *187*, 151.

[111] F. Årén, R. Andersson, A. A. Franco, P. Johansson, *J. Electrochem. Soc.* **2023**, *170*, 060506.

[112] G. Åvall, P. Johansson, *J. Chem. Phys.* **2020**, *152*, 234104.

[113] D. M. Seo, O. Borodin, D. Balogh, M. O'connell, Q. Ly, S.-D. Han, S. Passerini, W. A. Henderson, *J. Electrochem. Soc.* **2013**, *160*, A1061.

[114] O. Borodin, G. A. Giffin, A. Moretti, J. B. Haskins, J. W. Lawson, W. A. Henderson, S. Passerini, *J. Phys. Chem. C* **2018**, *122*, 20108.

[115] A. R. Yusupova, E. V. Kuzmina, V. S. Kolosnitsyn, *J. Phys. Chem. B* **2022**, *126*, 7676.

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[116] F. Chen, X. Wang, M. Armand, M. Forsyth, *Nat. Mater.* **2022**, *21*, 1175.

[117] C. A. Vincent, *Electrochim. Acta* **1995**, *40*, 2035.

[118] P. G. Bruce, A. Lisowska-Oleksiak, C. A. Vincent, *J. Electroanal. Chem.* **1995**, *384*, 85.

[119] J. Evans, C. A. Vincent, P. G. Bruce, *Polymer (Guildf)* **1987**, *28*, 2324.

[120] A. D. Khudyshkina, A. J. Butzelaar, Y. Guo, M. Hoffmann, T. Bergfeldt, M. Schaller, S. Indris, M. Wilhelm, P. Théato, F. Jeschull, *Electrochim. Acta* **2023**, *454*, 142421.

[121] R. Dugas, J. D. Forero-Saboya, A. Ponrouch, *Chem. Mater.* **2019**, *31*, 8613.

[122] D. A. Gribble, L. Frenck, D. B. Shah, J. A. Maslyn, W. S. Loo, K. I. S. Mongcopa, D. M. Pesko, N. P. Balsara, *J. Electrochem. Soc.* **2019**, *166*, A3228.

[123] M. P. Rosenwinkel, R. Andersson, J. Mindemark, M. Schönhoff, *J. Phys. Chem. C* **2020**, *124*, 23588.

[124] R. Andersson, G. Hernández, J. Mindemark, *Phys. Chem. Chem. Phys.* **2022**, *24*, 16343.

[125] J. Barthel, R. Buchner, P.-N. Eberspächer, M. Münsterer, J. Stauber, B. Wurm, *J. Mol. Liq.* **1998**, *78*, 83.

[126] P. A. R. D. Jayathilaka, M. A. K. L. Dissanayake, I. Albinsson, B.-E. Mellander, *Electrochim. Acta* **2002**, *47*, 3257.

[127] G. Pagot, K. Vezzù, C. S. Martinez-Cisneros, C. Antonelli, B. Levenfeld, A. Varez, J.-Y. Sanchez, V. Di Noto, *ChemElectroChem* **2021**, *8*, 2459.

[128] M. Salama, I. Shterenberg, L. J. W. Shimon, K. Keinan-Adamsky, M. Afri, Y. Gofer, D. Aurbach, *J. Phys. Chem. C* **2017**, *121*, 24909.

[129] M. Gouverneur, J. Kopp, L. Van Wüllen, M. Schönhoff, *Phys. Chem. Chem. Phys.* **2015**, *17*, 30680.

[130] J. D. Forero-Saboya, D. S. Tchitchekova, P. Johansson, M. R. Palacín, A. Ponrouch, *Adv. Mater. Interfaces* **2022**, *9*, 2101578.

[131] Z. Li, J. Häcker, M. Fichtner, Z. Zhao-Karger, *Adv. Energy Mater.* **2023**, *13*, 2300682.

[132] H. R. Tinker, C. A. Howard, M. Zhou, Y. Xu, *Mater. Adv.* **2023**, *4*, 2028.

[133] A. M. Melemed, B. M. Gallant, *J. Electrochem. Soc.* **2020**, *167*, 140543.

[134] F. Tuerxun, K. Yamamoto, M. Hattori, T. Mandai, K. Nakanishi, A. Choudhary, Y. Tateyama, K. Sodeyama, A. Nakao, T. Uchiyama, M. Matsui, K. Tsuruta, Y. Tamenori, K. Kanamura, Y. Uchimoto, *ACS Appl. Mater. Interfaces* **2020**, *12*, 25775.

[135] A. Baskin, D. Prendergast, *J. Phys. Chem. C* **2016**, *120*, 3583.

[136] M. Vittadello, D. I. Waxman, P. J. Sideris, Z. Gan, K. Vezzù, E. Negro, A. Safari, S. G. Greenbaum, V. Di Noto, *Electrochim. Acta* **2011**, *57*, 112.

[137] S. S. R. K. C. Yamijala, H. Kwon, J. Guo, B. M. Wong, *ACS Appl. Mater. Interfaces* **2021**, *13*, 13114.

[138] F. Tuerxun, K. Yamamoto, T. Mandai, Y. Tateyama, K. Nakanishi, T. Uchiyama, T. Watanabe, Y. Tamenori, K. Kanamura, Y. Uchimoto, *J. Phys. Chem. C* **2020**, *124*, 28510.

[139] F. Bertasi, C. Hettige, F. Sepehr, X. Bogle, G. Pagot, K. Vezzù, E. Negro, S. J. Paddison, S. G. Greenbaum, M. Vittadello, V. Di Noto, *ChemSusChem* **2015**, *8*, 3069.

[140] Y. Zhao, A. Du, S. Dong, F. Jiang, Z. Guo, X. Ge, X. Qu, X. Zhou, G. Cui, *ACS Energy Lett.* **2021**, *6*, 2594.

[141] R. Lv, X. Guan, J. Zhang, Y. Xia, J. Luo, *Natl. Sci. Rev.* **2020**, *7*, 333.

[142] B. Yang, L. Xia, R. Li, G. Huang, S. Tan, Z. Wang, B. Qu, J. Wang, F. Pan, *J. Mater. Sci. Technol.* **2023**, *157*, 154.

[143] J. Zhang, X. Guan, R. Lv, D. Wang, P. Liu, J. Luo, *Energy Storage Mater.* **2020**, *26*, 408.

[144] A. Ponrouch, D. Tchitchekova, C. Frontera, F. Bardé, M. E. A.-D. Dompablo, M. R. Palacín, *Electrochem. Commun.* **2016**, *66*, 75.

[145] Z. Zhao-Karger, Y. Xiu, Z. Li, A. Reupert, T. Smok, M. Fichtner, *Nat. Commun.* **2022**, *13*, 3849.

[146] A. Patrick, M. Glasse, R. Latham, R. Linford, *Solid State Ionics* **1986**, *18*, 1063.

[147] R. Schöllhorn, H. Meyer, *Mater. Res. Bull.* **1974**, *9*, 1237.

[148] M. S. Whittingham, *Science (80-.)* **1976**, *192*, 1126.

[149] M. Gauthier, D. Fauteux, G. Vassort, A. Bélanger, M. Duval, P. Ricoux, J.-M. Chabagno, D. Muller, P. Rigaud, M. B. Armand, D. Deroo, *J. Electrochem. Soc.* **1985**, *132*, 1333.

[150] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724.

[151] M. Smeu, M. S. Hossain, Z. Wang, V. Timoshevskii, K. H. Bevan, K. Zaghib, *J. Power Sources* **2016**, *306*, 431.

[152] C. D. Wessells, S. V. Peddada, M. T. Mcdowell, R. A. Huggins, Y. Cui, *J. Electrochem. Soc.* **2011**, *159*, A98.

[153] R. Y. Wang, B. Shyam, K. H. Stone, J. N. Weker, M. Pasta, H. W. Lee, M. F. Toney, Y. Cui, *Adv. Energy Mater.* **2015**, *5*, 1.

[154] N. Kuperman, P. Padigi, G. Goncher, D. Evans, J. Thiebes, R. Solanki, *J. Power Sources* **2017**, *342*, 414.

[155] A. L. Lipson, S.-D. Han, S. Kim, B. Pan, N. Sa, C. Liao, T. T. Fister, A. K. Burrell, J. T. Vaughey, B. J. Ingram, *J. Power Sources* **2016**, *325*, 646.

[156] T. Shiga, H. Kondo, Y. Kato, M. Inoue, *J. Phys. Chem. C* **2015**, *119*, 27946.

[157] C. Sångeland, R. Younesi, J. Mindemark, D. Brandell, *Energy Storage Mater.* **2019**, *19*, 31.

[158] J. Mindemark, R. Mogensen, M. J. Smith, M. M. Silva, D. Brandell, *Electrochem. Commun.* **2017**, *77*, 58.

[159] A. D. Khudyshkina, P. A. Morozova, A. J. Butzelaar, M. Hoffmann, M. Wilhelm, P. Theato, S. S. Fedotov, F. Jeschull, *ACS Appl. Polym. Mater.* **2022**, *4*, 2734.

[160] J. Bitenc, K. Pirnat, T. Bancic, M. Gaberscek, B. Genorio, A. Randon-Vitanova, R. Dominko, *ChemSusChem* **2015**, *8*, 4128.

[161] T. Yamamoto, H. Etori, *Macromolecules* **1995**, *28*, 3371.

[162] G. Hernández, N. Casado, R. Coste, D. Shanmukaraj, L. Rubatat, M. Armand, D. Mecerreyes, *RSC Adv.* **2015**, *5*, 17096.

[163] G. Hauffman, J. Rolland, J.-P. Bourgeois, A. Vlad, J.-F. Gohy, *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 101.

[164] Z. Song, H. Zhan, Y. Zhou, *Angew. Chem., Int. Ed.* **2010**, *49*, 8444.

[165] M. E. Baumert, V. Le, P.-H. Su, Y. Akae, D. Bresser, P. Théato, M. M. Hansmann, **2023**, *145*, 23334.

[166] M. Sotoudeh, A. Groß, *JACS Au* **2022**, *2*, 463.

[167] L. M. Ghiringhelli, J. Vybiral, S. V. Levchenko, C. Draxl, M. Scheffler, *Phys. Rev. Lett.* **2015**, *114*, 105503.