Alternatives to fluorinated binders: recyclable copolyester/carbonate electrolytes for high-capacity solid composite cathodes†

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Optimising the composite cathode for next-generation, safe solid-state batteries with inorganic solid electrolytes remains a key challenge towards commercialisation and cell performance. Tackling this issue requires the design of suitable polymer binders for electrode processability and long-term solid–solid interfacial stability. Here, block-polyester/carbonates are systematically designed as Li-ion conducting, high-voltage stable binders for cathode composites comprising of single-crystal LiNi0.8Mn0.1Co0.1O2 cathodes, Li6PS5Cl solid electrolyte and carbon nanofibres. Compared to traditional fluorinated polymer binders, improved discharge capacities (186 mA h g−1) and capacity retention (96.7% over 200 cycles) are achieved. The nature of the new binder electrolytes also enables its separation and complete recycling after use. ABA- and AB-polymeric architectures are compared where the A-blocks are mechanical modifiers, and the B-block facilitates Li-ion transport. This reveals that the conductivity and mechanical properties of the ABA-type are more suited for binder application. Further, catalysed switching between CO2/epoxide A-poly carbonate (PC) synthesis and B-poly(carbonate-r-ester) formation employing caprolactone (CL) and trimethylene carbonate (TMC) identifies an optimal molar mass (50 kg mol−1) and composition (wPC 0.35). This polymer electrolyte binder shows impressive oxidative stability (5.2 V), suitable ionic conductivity (2.2 × 10−4 S cm−1 at 60 °C), and compliant viscoelastic properties for fabrication into high-performance solid composite cathodes. This work presents an attractive route to optimising polymer binder properties using controlled polymerisation strategies combining cyclic monomer (CL, TMC) ring-opening polymerisation and epoxide/CO2 ring-opening copolymerisation. It should also prompt further examination of polycarbonate/ester-based materials with today’s most relevant yet demanding high-voltage cathodes and sensitive sulfide-based solid electrolytes.

Introduction

Solid-state batteries (SSBs) have recently emerged as a promising follow-up technology to commercial lithium-ion batteries.1 Replacing liquid electrolytes in the latter for less flammable solid alternatives offers conceivably safer next-generation devices with higher energy densities and improved long-term performance.2,3 To this end, a significant research achievement was the discovery of inorganic solid electrolytes (such as Li6PS5Cl) with competitive ionic conductivities to liquids.4,5 Unlike liquids, however, maintaining intimate contact between the electrolyte and electrode particles is difficult.1,6 Optimising these solid interfaces is particularly key in the cathode given it comprises multiple solid phases and its proper function dictates attainable capacity and capacity retention.7–10 While advancements have been made, for instance using high-capacity nickel-rich manganese–cobalt oxides (NMC), most recently in single-crystal (sc) form,11–13 a suitable polymer binder is needed for large-scale fabrication and commercial use of cells.14–16

Typically, solid composite cathodes comprise a mixture of cathode particles, solid electrolyte, carbon and a polymer binder. The latter can hold solid phases together but also enables large-scale (i.e. roll-to-roll) electrode processability.15,16 Thus, they are an important consideration if solid-state battery technology is to be translated from the lab level to commercial development.17–19 In addition, elastomeric polymers can mitigate cathode volume changes during battery operation.20 The
added complexity of even small volume changes (6 vol% for LiNi0.8Mn0.1Co0.1O2 cathodes, NMC811) requires pressure to be applied to the cell for long-term capacity retention.\(^1\) For many reports, this is unrealistically high (\>50 MPa); acceptable cell pressures are 1–2 MPa or ideally lower.\(^1\)

So far, traditional rubber binders (nitrile butadiene, NBR and styrene butadiene, SBR), require modification with polar functionalities to impart adhesiveness for appreciable cycling stability.\(^2\) For cathode composites integrating Li6PS5Cl, this prevents standard wet slurry-based cathode fabrication, owing to the poor compatibility of Li6PS5Cl with polar solvents.\(^23–24\) However, recent findings summarised by Lu et al. suggest dry-processed electrodes may be better for both performance and sustainability by reducing solvent use.\(^25\) Currently, polytetrafluoroethylene (PTFE) is the prevalent binder for producing these solvent-free cathode composites but alongside also commonly used polyvinylidene fluoride (PVDF) cathode binders, fluorinated polymers pose significant environmental concerns.\(^26–27\) Consequently, fluorinated substances are proposed to be banned by the EU following a recommendation by the European Chemicals Agency.\(^28\) Besides, given that providing effective pathways for ions is fundamental for maximising cathode capacity, the inherent non-conductive nature of these and most binders is also limiting.\(^29\) Indeed, recent work demonstrates that chemically modifying PTFE with ionomers to impart even modest ionic conductivities (1.6 \(\times\) 10\(^{-5}\) S cm\(^{-1}\) at 25 °C) results in a 20% capacity gain over PTFE.\(^30\)

Clearly, alternative polymer binders are needed to meet the demanding requirements for high-capacity cathode composites in solid-state batteries.\(^31\) Fluorinated binders offer high electrochemical stability and finding replacements will require identifying less environmentally persistent polymers with high-voltage stability.

Here, we propose all polycarbonate/ester-based polymers as high-voltage stable, ionically conducting binders. Poly(tri-methylene carbonate), PTMC and poly(caprolactone), PCL are well-studied polycarbonate and polyester electrolytes, respectively.\(^32–35\) Of particular note are random copolymers of TMC and Cl\(_2\), P(CL-r-TMC) first reported by Mindemark et al. whereby a 1:4 ratio of TMC:Cl\(_2\) (20 mol% TMC) delivers optimal ionic conductivity (4.1 \(\times\) 10\(^{-5}\) S cm\(^{-1}\) at 25 °C) due to disruption of PCL crystallinity.\(^36–40\) Specifically for their role as solid-state composite cathode binders, these Li-ion conductors are revered for their high oxidative stability \((\geq 4.5–5 \text{ V})\), placing them in the right range for use with NMC.\(^41–43\) Additionally, ester/carbonate linkages are known to enable recyclability to monomers which can be initiated by the addition of catalysts, heat and/or manipulation of reaction conditions.\(^44–47\)

On its own, P(CL-r-TMC) is a soft (low \(T_g\)) amorphous polymer. To modify the mechanical properties for optimal binder performance including accommodating volume changes caused by internal stresses at higher voltages, hard \((\text{high } T_g)\) polymer blocks need to be introduced.\(^23,48–51\) Preparing phase-separated AB- or ABA-type block polymers (where A = hard and B = soft polymer) is a popular strategy where predictable microstructures correlate with particular mechanical behaviours.\(^22\) This study uses poly(4-vinyl cyclohexene carbonate) (PC) A-blocks as mechanical modifiers: whilst being a hard block, it is also oxygenated so may contribute towards Li-ion conductivity and its synthesis can sequester CO\(_2\).

**Results and discussion**

To prepare poly(carbonate-\(\text{block-ester}\)) binders featuring an ionically conducting P(CL-r-TMC) (B-block) combined with a PC mechanical modifier (A-block), a form of switchable polymerisation catalysis was selected (Fig. 1a).\(^23,51–57\) From a monomer...
mixture, this process applies a single catalyst (Scheme S1†) to direct polymerisations between lactone (CL)/cyclic carbonate (TMC) ring-opening polymerisation (ROP) and epoxide (vCHO)/CO₂ ring-opening copolymerisation (ROCOPI) by the presence/absence of CO₂ (Scheme S2†, S3, S4†). These switchable polymerisations are well-controlled, so the catalysis can be manipulated to systematically vary the polymer composition (A:B ratio), molar mass (Mₙ) and architecture. As such, this approach is attractive for designing new polymer binders as these parameters are expected to influence successful binder function.

To control the architecture, two different alcohol initiators were used; these react rapidly in situ with the catalyst (Scheme S1†).

When applied with bifunctional alcohol, 1,4-benzenedimethanol (BDM), ABA triblock polymers are accessed. Whereas monofunctional alcohol, 4-methyl benzyl alcohol (Me-BnOH) yields AB polymers (Schemes S3 and S4†). To control the Mₙ and A:B ratio, the ratio of [CL + TMC]₀ was adjusted with respect to the initiator, and the monomer conversions were varied (Table S1†). Accordingly, three systematic series of polymers were synthesised (Fig. 1b): Series I are AB (diblock) polymers with fixed A-block content expressed as a weight fraction, wᵥᵥ = 0.5, but variable overall molar masses, Mₙ (35–66 kg mol⁻¹); Series II are ABA (triblock) polymers with similarly fixed wᵥᵥ = 0.5 and variable molar masses, Mₙ (26–69 kg mol⁻¹); Series III feature ABA polymers with fixed molar mass (50 kg mol⁻¹) but variable A-block content (0.26–0.62) (Table 1). Henceforth, the polymers are labelled as ABA/AB (Mₙ, wᵥᵥ). In all cases, the targeted 1 : 4 TMC : CL ratio of the B-block (set by the monomer feed) was verified by reaction aliquots taken just before CO₂-triggered switching to vCHO/CO₂ ROCOP (Fig. S1†). As mentioned earlier, this ratio is favourable for suppressing PCL crystallinity which is important to maximise conductivity. The polymers were readily isolated in good yield (>75%) by precipitation from methanol and both the purity and compositions were confirmed by NMR spectroscopy (Fig. S2–S5†).

Table 1 Poly(carbonate-b-esters) and their data

<table>
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<tr>
<th>Series</th>
<th>Polymer</th>
<th>Mₙ (kg mol⁻¹)</th>
<th>wᵥᵥ</th>
<th>Tᵥᵥ</th>
<th>Tᵥᵥ</th>
<th>(°C)</th>
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<td>84</td>
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<td>AB (45, 0.47)</td>
<td>45</td>
<td>0.47</td>
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<td>102</td>
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<tr>
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<td>AB (69, 0.58)</td>
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<td>AB (35, 0.52)</td>
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<td>0.52</td>
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<tr>
<td>II</td>
<td>AB (44, 0.53)</td>
<td>44</td>
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<tr>
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<td>48</td>
<td>100</td>
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<td>AB (51, 0.26)</td>
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<td>III</td>
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<td>III</td>
<td>AB (50, 0.47)</td>
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See Fig. 1 for Series I–III descriptors. Polymers labelled as ABA/AB (Mₙ, wᵥᵥ) where Mₙ = overall molar mass in kg mol⁻¹ and wᵥᵥ = weight fraction of C. Determined by °H NMR spectroscopy of the purified polymer: initiator, PC (5.76 ppm) and P(CL−r-TMC) (2.00, 1.38 ppm) vs. 1,4-BDM (7.34 ppm) or Me-BnOH (7.17 ppm). Tᵥᵥ with 17 wt% LiTFSI from DSC where Tᵥᵥ corresponds to P(TMC−r-CL) and Tᵥᵥ to PC.

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polymers form a common microstructure which maximises ion transport. Small-angle X-ray scattering (SAXS) measurements confirmed this hypothesis since ABA (50, 0.30) and ABA (50, 0.35) formed weakly-ordered microstructures; either body-centred cubic or hexagonal (Fig. 2c and S14†). It is feasible that these microstructures provide channels that accelerate ion transport (Fig. 2d). This is consistent with work conducted by Balsara and co-workers which showed that for PS-b-PEO electrolytes, weakly ordered morphologies improved conductivity.51

From this systematic investigation of block polymer parameters, the optimal ionic conductivity was identified for ABA (50, 0.35) of 2.2 × 10^{-4} S cm^{-1} at 60 °C (Fig. 3a). Subsequently, this polymer formed the focus of the forthcoming investigations. From VFT analysis, the barrier for ion transport was favourably low, with an activation energy of 17.4 (±0.7) kJ mol^{-1} (Fig. S13†). We attribute this low barrier to both blocks being able to coordinate Li-ions, the occurrence of which is consistent with the presence of two resonances in the solid-state $^7$Li NMR spectroscopy (deconvolution given in Fig. 3b). By comparing against spectra collected for the constituent homopolymers, these resonances are assigned to the PC and P(CL-r-CL) B-block. (b) Ionic conductivity with variable A-content ($w_{PC}$) for ABA polymers with constant $M_n = 50$ kg mol^{-1}. (c) SAXS data for as-prepared ABA (50, $w_{PC}$)/17 wt% LiTFSI polymer systems. (d) ABA (50, 0.35) electrolyte film and schematic illustration of phase-separation behaviour. Nanostructure domain spacing, $d$ is estimated from the principal scattering peak ($q^*$) in the SAXS pattern ($d = 2\pi/q^*$). For all conductivity measurements, shading or error bars represent standard error for $N = 3$ repeats.

Fig. 2 (a) (Top) $M_n$-dependence of ionic conductivity ($\sigma$) at $T = 30$ °C for AB vs. ABA polymers/17 wt% LiTFSI at fixed $w_{PC} = 0.5$. (Bottom) Corresponding DSC $T_g$ values for P(TMC-r-CL) B-block. (b) Ionic conductivity with variable A-content ($w_{PC}$) for ABA polymers with constant $M_n = 50$ kg mol^{-1}. (c) SAXS data for as-prepared ABA (50, $w_{PC}$)/17 wt% LiTFSI polymer systems. (d) ABA (50, 0.35) electrolyte film and schematic illustration of phase-separation behaviour. Nanostructure domain spacing, $d$ is estimated from the principal scattering peak ($q^*$) in the SAXS pattern ($d = 2\pi/q^*$). For all conductivity measurements, shading or error bars represent standard error for $N = 3$ repeats.
stress–strain behaviour of ABA (50, 0.35)/LiTFSI supported the formation of a stretchable material that can repeatably recover after stress is applied and removed (Fig. S18†). In comparison, PTFE samples, prepared equivalently, showed very low elastic recovery and were not elastomeric (Fig. S19†). Peel force testing, on alumina, using ABA (50, 0.35)/LiTFSI also showed promising adhesive properties with a peel force of 0.45 N mm$^{-1}$ (Fig. S20†). The adhesive properties are comparable to a previously reported series of polycarbonate-$b$-ether-$b$-carbonate binders for solid state batteries.$^{56}$

Before cell fabrication, the viscoelastic properties of ABA (50, 0.35)/LiTFSI were also probed by temperature and frequency sweep rheological experiments. The elastic properties, expressed as the shear storage modulus ($G'$), and the viscosity, related to the loss modulus ($G''$), were observed to crossover ($G' = G''$) at 73 °C (Fig. 4a). Below this temperature, the Li-ion conducting binder behaves as an elastic solid with a low value of $G'$ (2–0.2 MPa), resulting in a soft, more resilient polymer filler. Above this temperature and at sufficiently slow shear rates (<0.2 Hz (Fig. 4b and S21†)), the binder becomes processable. This is a very accessible processing window compared to for example PTFE binders, which have very high melting temperatures.$^{66}$

Subsequently, the ABA (50, 0.35)/LiTFSI polymer electrolyte film could be cryo ball milled to produce a fine powder and dried mixed into a free-standing composite cathode. The polymer was integrated in 5 wt% with high-performance cathode material sc-NMC811, ceramic electrolyte Li$_6$PS$_5$Cl and carbon nanofibre,

![Fig. 3](a) Temperature-dependence of ionic conductivity for ABA (50, 0.35)/17 wt% LiTFSI. (b) Solid-state $^7$Li NMR spectrum with peak deconvolution to PC and P(CL-$\alpha$-TMC) phases. (c) Oxidative stability vs. Li metal and stainless-steel counter electrode measured by LSV at 60 °C, 0.1 mV s$^{-1}$ scan rate. (d) CV at 0.5 mV s$^{-1}$ scan rate recorded over 35 cycles.

![Fig. 4](Viscoelastic mechanical properties for ABA (50, 0.35)/LiTFSI. (a) Temperature-dependence of $G'$ and $G''$. (b) Master curve of the frequency dependence of $G'$ and $G''$.)

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CNF, in a 70 : 23 : 2 wt% ratio (Fig. 5a). Evidence of sufficient mixing of the cathode components was evaluated by SEM/XPS (Fig. S22 and S23†). The resulting cathode composite was then densified at 250 MPa, before being assembled into a full solid-state cell with a Li4Ti5O12 (LTO) anode and Li6PS5Cl solid electrolyte. LTO was chosen due to its superior power density to graphite and its chemical and electrochemical stability with Li6PS5Cl.

To evaluate the binder performance, the cell was then cycled at 60 °C using a low 1 MPa applied pressure (Fig. 5b, c and S24,† areal capacity = 3 mA h cm⁻²). A high initial discharge capacity of 186 mA h g⁻¹ was observed compared to 177 mA h g⁻¹ with analogous cells prepared with PTFE binder. As in previous studies, we investigated the new binder with both FSI and TFSI anions. Whereas the capacity with the TFSI anion declined with the number of charge/discharge cycles (73% retention after 200 cycles), this was not observed with FSI which resulted in 96.7% after 200 cycles (Fig. 5b, c and S25†). This could be attributed to the TFSI anion forming unstable interphases with the cathode.⁶⁸,⁶⁹ Further detailed investigations of this inorganic chemistry will form the focus of subsequent work. Regardless, this high cycling stability with LiFSI whilst still delivering a good initial capacity (183 mA h g⁻¹) is promising. In particular, it outperforms those obtained with PTFE binder, which retains 86.4% capacity over 200 cycles starting at 177 mA h g⁻¹ (Fig. 5b and c). This can be attributed to the ionic conductivity and mechanical properties of the ABA (50, 0.35) electrolyte; PTFE is neither conductive nor elastomeric.¹⁷ Furthermore, the composite cathode also showed a superior coulombic efficiency of >99.7% (Fig. S26†). When cycled at 30 °C, the cell had a lower initial discharge capacity (111 mA h g⁻¹); this could be optimised as part of further work (Fig. S27†).

Fig. 5  (a) Fabrication of composite cathode and solid-state cell configuration, LTO|Li6PS5Cl|NMC–PE composite. (b) Specific discharge capacity vs. cycle number at T = 60 °C, 1 MPa stack pressure, 1 mA cm⁻². (c) Initial discharge capacity, and capacity retention after 200 cycles (labelled).

Fig. 6  Chemical recycling of the polymer electrolyte binder, catalysed by Zn(Oct)₂/GEO ([Zn(Oct)₂]:[GEO]:[polymer]₀ = 1 : 1.13 : 1000) at 200 °C. Monomers were recovered by distillation under 1 mbar pressure, with the mixture heated to 200 °C. (a) Schematic depicting how the polymer binder can be recovered from the cell. (b) Polymer degradation vs. time, throughout the chemical recycling process. (c) The monomers recovered in the chemical recycling process.
Lastly, given the promising cell performances, proof-of-principle chemical recycling of the polymer electrolyte binder to component monomers was explored.\textsuperscript{45,47} The polymer was extracted from the composite with toluene (Fig. 6a). Although this is also achievable with fluorinated binders, it typically requires harsher solvents, namely NMP. Furthermore, these polar solvents will likely result in breakdown of the Li$_6$PS$_5$Cl ceramic electrolyte. Next, catalysed depolymerisation of a pure sample of ABA (50, 0.35) was demonstrated and at 200 °C allowed for 90% recovery of monomers after 16 h (Fig. 6b, S26, Scheme S5, see ESI for optimised depolymerisation conditions\textsuperscript{†}); such depolymerisation is not possible with PTFE. The depolymerisation resulted in 90% conversion to small molecules, which were identified using spectroscopy. These molecules were the recovered monomers vCHO, TMC and CL, and a cyclic carbonate which is also a potential monomer for poly-carbonates. These monomers were formed in the expected ratios based on the polymer composition (Fig. 6c and Table S5). The 10% residual mass is attributed to a small amount of crosslinked polymer, likely formed at higher temperatures via reactions between the vinyl groups (N.B. experiments were conducted using neat polymer). Also observed by FTIR and NMR analyses was trans-cyclic carbonate which can be polymerised to the analogous polycarbonate as that produced from vCHO/CO$_2$ ROCOP (Scheme S7).\textsuperscript{79} Further separation of the monomers is unnecessary as the switch catalysis used to make these polymers works from a mixture of monomers, with the introduction of CO$_2$ triggering the formation of the A-block polymers.

Conclusions

A series of ABA- and AB-block polymers, where A = poly(vinyl cyclohexene carbonate) (PC), and B = poly(c-caprolactone-γ-tri-methylene carbonate) ([P(CL-γ-TMC)]) were tested as polymer electrolyte binders for solid composite cathodes. The polymers were prepared using a one-pot, one-catalyst switchable polymerisation allowing for control over the molar mass, composition and end-group chemistry. This allowed systematic investigations of the polymer structure (AB vs. ABA), molar mass (26 < $M_n$ < 69 kg mol$^{-1}$) and PC-block content (0.26 < A-block content < 0.62). The best electrolyte, comprising ABA-polymer and lithium salt, showed high oxidative stability allowing for use with high-capacity cathodes (5.2 V), good Li-ion conductivity (2.2 × 10$^{-4}$ S cm$^{-1}$ at 60 °C) and viscoelastic behaviour. As such, the polymer was a compatible binder with a leading cathode (scNMC811) and an inorganic solid electrolyte (Li$_6$PS$_5$Cl). The resulting full solid-state cell capacities were high, measuring 186 mA h g$^{-1}$, and showed impressive capacity retention of 96.7% over 200 cycles. These results outperformed the use of PTFE, which is the leading binder for dry-processed solid-state composites, resulting in capacities of 177 mA h g$^{-1}$ and 86.4% capacity retention over 200 cycles. Moreover, chemical recycling of the polyester/carbonate binder allowed for 90% monomer recovery, establishing a route to cell component recycling. Overall, these polymers are an alternative to currently relied-upon fluorinated polymers, which have growing associated environmental concerns.

Finally, establishing commercial solid-state batteries demands improved performance of the cathode. Switchable polymerisation is an excellent tool for the ongoing optimisation of composite electrodes, via polymeric binder design. There is a wealth of commercial monomers available which apply to this approach and thus are capable of leading to diverse, heteroatom-rich, therefore Li-ion conductive, polymeric binders.

Author contributions

HY, HG, KY, TM and GJR: investigation, methodology, validation, formal analysis, data curation. GLG, MP, PGB and CKW: conceptualization, supervision, funding acquisition, writing.

Conflicts of interest

CKW is a director of Econic Technologies.

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References