



Full Paper

Fast-charging all-solid-state battery cathodes with long cycle life

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ARTICLE INFO

Keywords:

Fast-charging

All-solid-state battery

Cathode design

Three-electrode

High current density

Sulfide solid electrolyte

ABSTRACT

Many battery applications target fast charging to achieve an 80 % rise in state of charge (SOC) in < 15 min. However, in the case of all-solid-state batteries (SSBs), they typically take several hours to reach 80 % SOC while retaining a high specific energy of 400 W h kg_{cell}⁻¹. We specify design strategies for fast-charging SSB cathodes with long cycle life and investigate the fast-charging capability of a sulfide-based single crystal Li-Ni-Mn-Co oxide composite cathode. At 30 °C and charging at 15 mA cm⁻², a specific capacity of 150 mA h g⁻¹ was achieved in ~8 min, with 81 % capacity retention after 3000 cycles. Critically, a 3-electrode arrangement was used to avoid the common problem of overcharging at high current densities. By following the design strategy and optimized manufacturing, a 210 μm thick cathode was able to be charged at an extraordinary current density of 50 mA cm⁻² to reach an areal capacity of 8 mA h cm⁻² in only 10 min, suggesting practical cathodes for SSBs with 400 W h kg_{cell}⁻¹ may be within reach.

1. Introduction

Solid-state batteries (SSBs) have the potential to be safer and have higher specific energy than conventional Li-ion batteries (LIBs) because they use (i) an inorganic solid electrolyte (SE) instead of a flammable liquid electrolyte (LE), and (ii) Li metal instead of a graphite intercalation anode [1–3]. Sulfide SEs with a high ionic conductivity beyond 1 mS cm⁻¹ and favorable thermomechanical fabrication properties facilitate large-scale SSB manufacturing at room temperature, a major advantage over lower conductivity oxide SEs that require higher temperature processing [4–10]. Although SSBs with high specific energy > 400 W h kg_{cell}⁻¹ at room temperature have been demonstrated, they suffer from long charging times (e.g. cycling at only C/10 to reach full charge after 10 h) deriving from a low current density < 1 mA cm⁻² that is required to avoid Li dendrite formation and short circuits [11]. A high external uniaxial stack pressure (>5 MPa) is also usually required to maintain the integrity of SE-active material interfaces during cycling [12–14]. Even with these restrictions, SSB capacity nonetheless usually fades significantly during cycling and there is low (<70 %) cathode active material (CAM) utilization [15]. In contrast, many practical

applications require relatively short charging times and therefore comparatively high charging current densities [16]. For example, in the case of electric vehicles (EVs), miles of range per charging time relates directly to the charge current density, and a desirable EV battery charging time of < 15 min (4 C) at a practical cathode capacity of 3 mA h cm⁻² requires a current density of > 10 mA cm⁻² [12,17].

Unfortunately, current densities of this magnitude have scarcely been demonstrated, even at elevated temperatures (e.g. 60 °C) [5,18,19] that are used to speed up otherwise relatively slow electrochemical reactions and ionic diffusion. For example, sulfide SE-based lithium cobalt oxide (LCO) 28 μm thick composite cathodes (CAM loading: 4.9 mg cm⁻²) with a lithium titanium oxide (LTO) anode were charged and discharged at 12 mA cm⁻² (18 C) at 100 °C [5]. More recently, charge current densities of ~10 mA cm⁻² were explored in lithium nickel cobalt oxide (NMC) and sulfide SE cathodes, which again used high temperatures ≥ 55 °C and/or high stack pressures ≥ 50 MPa [20, 21].

Assuming a focus on cathode performance for an EV fast charge of < 15 min, a relatively thick (>70 μm) electrode with a high CAM areal loading (>15 mg cm⁻²) and a high cycle life (maximum 80 % capacity

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fade over 1000 cycles) will typically be required [22–24]. To reach these targets, the composite CAM/SE cathode must not only be designed to have excellent ionic and electronic percolation but also comprise materials with slow degradation over many cycles.

Whereas parameter variations to optimize cathode performance have been investigated individually, these various insights have not previously been combined to arrive at a set of design rules, or selection criteria, for a cathode performance focused on fast charging and long cycle life [25,26]. In other words, there is a gap in how to combine holistically the design criteria that are now emerging rapidly. These are proposed as follows: (i) Single crystal (SC) instead of polycrystalline CAM to avoid pulverization strains and capacity fade [27–29], (ii) small ($< 5 \mu\text{m}$) CAM particles for sufficiently fast intercalation kinetics and to promote electronic percolation [30], (iii) a restricted range of charge to ensure a low ($< 3\%$) volume change of the CAM during cycling to decrease mechanical degradation by pulverization [31], (iv) carbon nanofibers (CNF) instead of carbon black (CB) for electronic percolation at lower fraction and reduced SE decomposition [32], (v) small ($< 1 \mu\text{m}$) SE particles to pack efficiently around the larger CAM particles and to ensure intimate interfacial contact [33], (vi) high intrinsic ionic conductivity of the SE ($> 1 \text{ mS cm}^{-1}$) for fast Li-ion transport [22], (vii) homogeneous mixing of cathode components for improved ionic and electronic percolation, (viii) low ($< 10\%$) as-manufactured pore volume for low cathode impedance [34], and (ix) intact, crack-free CAM particles after densification and before cycling [28].

Here we investigate composite cathodes that conform to the design criteria in a three-electrode arrangement that allows the underlying cathode performance to be disentangled from any overpotential restrictions at the anode. We find that fast-charging times < 10 min can be achieved in an argyrodite electrolyte-based SC-NMC composite cathode at 15 mA cm^{-2} and 30°C with a high capacity of 150 mA h g^{-1} , representing a CAM utilization of 71 %. Capacity retention after 3000 cycles was 81 % and voided volume in the composite cathode increased from 3 % to 6.9 % after 1000 cycles. Finally, $210 \mu\text{m}$ thick cathodes were charged at 50 mA cm^{-2} and 80°C in only 10 min corresponding to an areal capacity of 8 mA h cm^{-2} . The cell performance demonstrates that fast charging can be realized in practical SSB cathode thicknesses even at room temperature. Where applications allow asymmetric charge/discharge times, we show that optimized composite cathodes can make a valuable contribution to SSBs with practical charge times and cycle lives.

2. Materials and methods

2.1. Cathode preparation

Commercial powders of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ (MSE Supplies), $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI, MSE Supplies, Pass 325 mesh, synthesized from $> 99.9\%$ precursor materials) solid electrolyte, and carbon nanofibers (Sigma-Aldrich, pyrolytically stripped, $> 98\%$ carbon based, $D \times L$ $100 \text{ nm} \times 20\text{--}200 \mu\text{m}$) were mixed in a Fritsch ball mill at a weight ratio of 70:27.5:2.5 (volume ratio: 44:52:4) and milled at 140 rpm for 30 min [35]. SC-NMC was chosen because it exhibits high mechanical integrity during cell manufacturing and cycling, with high intrinsic specific capacity [28]. Mean particle diameters for NMC and LPSCI were $\sim 3 \mu\text{m}$ and $\sim 1 \mu\text{m}$ respectively.

2.2. Cell assembly

Both 2-electrode and 3-electrode cells with identical composite cathodes were assembled. The 2-electrode cells were assembled by stacking a layer of LPSCI SE (30 mg to give a thickness of 1 mm) and a layer of the cathode mixture (4.2 mg and 12.6 mg to give 15 mA h cm^{-2} and 45 mA h cm^{-2}) in a polyether ether ketone (PEEK) mould and subsequently pressed at 500 MPa using a WC die set. Three-electrode cells were manufactured in a geometrically similar mould in which a

0.5 mm thick stainless-steel sheet was integrated in the center that acted as current collector for the reference electrode as shown in Fig. S1a. A $\sim 30 \mu\text{m}$ thick Li foil was attached to the stainless-steel sheet to act as a reference electrode before the mould was loaded with powder. To avoid any short circuits between the cathode, reference electrode, and anode, a thicker (3.3 mm) separator was realised from 100 mg sulfide SE. Cells for cathode pore evolution analysis were manufactured in a custom-made mould, shown in Fig. S1b that could be disassembled after cycling. To avoid early cell failure and quick Li dendrite formation, to raise the critical current density at the anode, and to allow the cathode to be studied for fast charge response, Li-In alloy anodes were used instead of pure Li [36]. Li-In anodes were capacity matched to the cathode loading and made from 1 to 3 stacks of $70 \mu\text{m}$ thick In foil and $30 \mu\text{m}$ thick Li foil, similarly to [37,38]. The anode stacks were placed on the SE pellet and pressed with a Cu current collector at 500 MPa for 5 min. An asymmetric stack pressure of 0.2 MPa on the cathode and 10 MPa on the anode was applied by combining a compression spring and a calibrated torque wrench allowing some compensation for cell volume changes as previously described [28,39]. Details of the stack pressure and stress state in the pellet are shown schematically in Fig. S2 and described in Note S1.

2.3. Cathode microstructure analysis

Scanning electron microscope (SEM)/energy-dispersive X-ray spectroscopy (EDX) was used to investigate the sulfide-based cathode cross-sections that were prepared using an automated Ar ion polishing system (PECS 2, Gatan) and transferred under vacuum into a Zeiss Merlin SEM using an airtight transfer device. Images were obtained using an in-lens secondary electron detector. EDX was carried out using an Oxford Instruments X-Max 150 silicon drift detector and analysis was conducted using AZtec software. An in-house developed design for cell/mould disassembly (Fig. S1b) was used to allow recovery of pristine and cycled cells from the PEEK mould that were then analyzed by a variety of techniques. A Thermo Scientific Helios G4 Plasma FIB Dual Beam (or P-FIB) system was used to study the microstructure changes of pristine and cycled composite cathodes. A large trench was firstly milled in bulk cells using a focused Xe^+ beam at 30 kV and $2.5 \mu\text{A}$ around the region of interest that provided space for any re-deposited milled material and avoided any shadow effects when obtaining SEM images. The milled cross-section was polished using a lower beam current from 60 nA down to 4 nA at 30 kV to remove FIB-induced roughness. ImageJ and Avizo software were used to process and generate 3D visualizations of the P-FIB datasets.

2.4. Electrochemical measurements

Three-electrode cells were used to precisely determine cathode charge/discharge capacities in rate tests and to accurately stop charging/discharging at 4.3 V/2.5 V vs. Li^+/Li , in order to avoid any form of undercharging or overcharging which would arise by simply guessing the cut-off voltage or translating voltage limits obtained at much lower unrepresentative current densities [40]. The measured charge/discharge capacities from the 3-electrode cells then served to inform the cut-off voltages applied to the 2-electrode cells. Two-electrode cells were used for all cycle life experiments and could make use of thinner separators than those used in the 3-electrolyte cells. Two-electrode cells were cycled using a constant current mode in a Bio-Logic SAS Model BCS-805. A constant voltage mode was purposefully avoided in order to reduce the amount of time that the materials were exposed to high voltage, which can promote faster degradation [29]. All average coulombic efficiencies (CEs) were calculated without the first cycle data. Three-electrode rate tests and three-electrode electrochemical impedance spectroscopy (EIS) (from 1 MHz to 0.1 Hz) were carried out using a Gamry 1000 potentiostat. Experimental details of the rate performance cell set-up including all relevant dimensions and exact

physical location of the reference electrode are shown schematically in Fig. S3 and described in Note S2. EIS was performed using a combination of the 2 and 3-electrode arrangements that are shown in Fig. S4, with typical Bode and Nyquist plots before cycling and after charge shown in Figs. S5 and S6 respectively. The equivalent circuit shown in Fig. S7 was used for fitting to the data of cells after cycling and accounted for resistances originating from the SE separator R_{SE} , the cathode R_{cat} , and the anode R_{an} .

3. Results

3.1. Fast-charging rate performance

Combining the design criteria (i) to (ix) above, a 3-electrode SSB according to Fig. 1a was constructed following the methods described in the experimental section. A cross-sectional SEM image and EDX map of a typical cathode is shown in Fig. S8 with the desired near-uniform distribution and high density of the constituents and no fractured CAM particles. Fig. 1b shows the charge and discharge voltage of the cathode vs. Li^+/Li with no contribution from the SE or the anode determined using a 3-electrode rate test at 30°C , as the charge current density increased from 1 to 15 mA cm^{-2} . This approach reveals any overpotentials at the composite cathode as the charging current density increases relate to kinetic constraints at the cathode only. For all cases, the discharge current density was kept constant at 1 mA cm^{-2} to ensure that the battery was always at a consistently low SOC before charging, which is why the voltage curves were similar at the beginning of charging. The

voltages differed at the beginning of discharge because there was a different initial SOC after charging, as a result of the sequence of different charging rates. The cathode voltage increased faster as charging continued because kinetic limitations in the composite cathode led to an increasingly growing overpotential. Fig. 1c shows the discharge capacity as a function of cycle number in a corresponding 2-electrode arrangement. The discharge capacity decreased from 196 ± 0.8 to $150 \pm 1.1\text{ mA h g}^{-1}$ as the charge current density was increased from 1 to 15 mA cm^{-2} i.e. from 3 h to 8 min. This indicated a high capacity retention of 76 %, and a high CAM utilization of 71 % at 30°C (assuming a theoretical capacity of 210 mA h g^{-1}).

When the discharge current density was increased together with the charge current density, as shown in Fig. S9a–b, there was a further reduction in discharge capacity because relatively low Li-ion diffusivity in the NMC during discharge led to a higher retained SOC (Table S1) at the end of the discharge cycle [41]. A constant discharge current density of 1 mA cm^{-2} here corresponded to a discharge time of $< 3\text{ h}$, which might be suitable for some applications including EVs. However, a charging time of $\sim 3\text{ h}$ is much less useful.

The coulombic efficiency (CE) in the first cycle was $81 \pm 0.3\%$ and $85 \pm 0.2\%$ at 1 mA cm^{-2} and 0.2 mA cm^{-2} , respectively, as shown in Fig. S9c–d, which compared favorably to the literature [29,42]. First cycle CEs in NMC-sulfide-based SSBs are typically $< 90\%$ because of sulfide SE decomposition or surface reactions of the active material, but typically increase for subsequent cycles [32,43]. The first cycle CE depended on current density because the discharge capacity dropped more than the charge capacity due to the intrinsic diffusivity of NMC

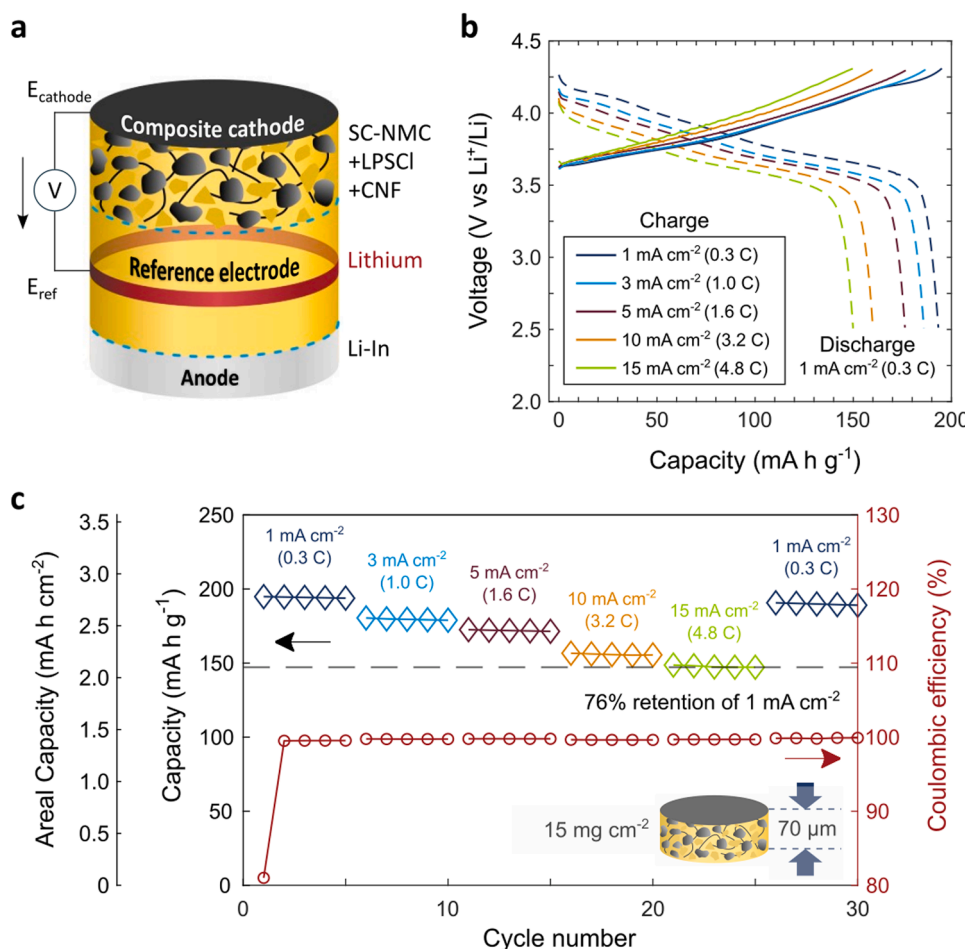


Fig. 1. Fast-charging rate performance (a) Schematic of the 3-electrode cell set-up used to measure (b) the voltage response vs. Li^+/Li (without first cycle) in a rate performance test at different charge current densities from 1 to 15 mA cm^{-2} , and constant discharge rate of 1 mA cm^{-2} at 30°C . (c) Discharge capacity and coulombic efficiency as a function of cycle number conducted in a 2-electrode arrangement.

that is lower during discharge than during charge [41].

After 25 cycles and reaching a current density of 15 mA cm^{-2} , the charge current density was reduced back to 1 mA cm^{-2} in Fig. 1c, and the initial capacity was almost fully retrieved. As cycling then continued there was no evidence of activation effects indicated by a temporary increase in capacity in the early stages of cycling [44]. Most usually this occurs when, unlike here, relatively high stack pressures are employed, which add some additional densification. Instead, there was a slow but steady decline in capacity at a constant current density, as shown in Fig. S10.

3.2. Fast-charging cycle performance

To simulate repetitive fast charging the cycle life of the composite cathode was investigated at a high charge current density of 15 mA cm^{-2} and a discharge current density of 5 mA cm^{-2} , corresponding to rates of 4.8 C and 1.6 C respectively. Fig. 2a shows the capacity fade and CE as a function of cycle number in a 2-electrode arrangement. After 3000 asymmetric 4.8 C/1.6 C cycles, the capacity reduced to $81 \pm 2 \%$ of the first cycle and CE increased to $> 99 \%$ per cycle. The first cycle CE was not included in data averaging because the cycle life test was conducted after the cycle profile shown in Fig. 1c had already been applied. The corresponding areal capacity in Fig. 2a reduced to $< 2 \text{ mA h cm}^{-2}$ and CAM utilization reduced from 67 % to 54 % over 3000 fast-charging cycles. This demonstrated that even after thousands of cycles, the SOC of the SSB cathode could still be increased by more than 50 % in $< 8 \text{ min}$.

To understand the capacity fade mechanism, we further analyzed the charging curves as a function of cycle number, shown in Fig. 2b. The curves shifted to higher voltages relatively quickly in the first 50 cycles and then remained more similar for the last 1000 cycles. Fig. 2b shows that this overpotential increase was similar at both the beginning (10 mA h g^{-1}) and towards the end (100 mA h g^{-1}) of the charging profile. This behaviour was consistent with a steady increase in ohmic resistance, arising from the formation of an interfacial layer of lower ionic conductivity at the SE/CAM interface [45–47]. The ohmic resistance increase in the cell inevitably led to a steady decrease in the

effective CAM cut-off voltage at higher cycle numbers, and the observed fading of capacity and reduced CAM utilization. In contrast, any contribution to capacity fading due to CAM ionic or electronic isolation, because of interfacial debonding and/or particle cracking, was less significant because voltage increases would be expected to become marked towards the end of charge [13]. These scenarios for the voltage/capacity curves for interfacial resistance increase or loss of CAM are shown schematically in Fig. 2c. The evolution of the cell impedance up to 1000 cycles is shown in Fig. S11. There was a progressive increase in the cathode interfacial resistance over cycling shown in Fig. 2d, with a slower increase after approximately 300 cycles. The absence of any discontinuous or catastrophic resistance increase suggested that the low axial stack pressures ($< 1 \text{ MPa}$) were effective in mitigating any substantial loss of LPSCl/NMC interfacial contact during cyclic NMC volume changes [14,29,48].

3.3. Evolution of the cathode microstructure and pore volume

A relatively low rate of mechanical degradation was confirmed by a combination of P-FIB depth milling, SEM imaging, and 3D image reconstruction [31,49]. SEM images were acquired in parallel planes every 100 nm of milled depth and then reconstructed to form the 3D images shown in Fig. 3a–c before cycling, and after 10 and 1000 cycles respectively (reconstructed 3D microstructures are available online in Videos S1–3). Using a gray level threshold, the pores were isolated in the images, and the pore volume before cycling estimated at 3 %, which underlined the efficacy of our combined materials selection and manufacturing approach. The pore volume increased with cycles because of the cyclic CAM volume change as previously reported [49]. The NMC particles may also slightly reorganize as they shrink during charge (de-lithiation), and their subsequent volume expansion during discharge (lithiation) may result in local stresses that cause mechanical debonding between particles. Nonetheless, the pore volume after 10 cycles increased only slightly to 3.6 % due to net CAM volume changes because of partial intercalation during discharge of Li-ions deintercalated during charge [50]. After 1000 cycles the pore volume increased to 6.9 % (Fig. 3c), but nonetheless represented a

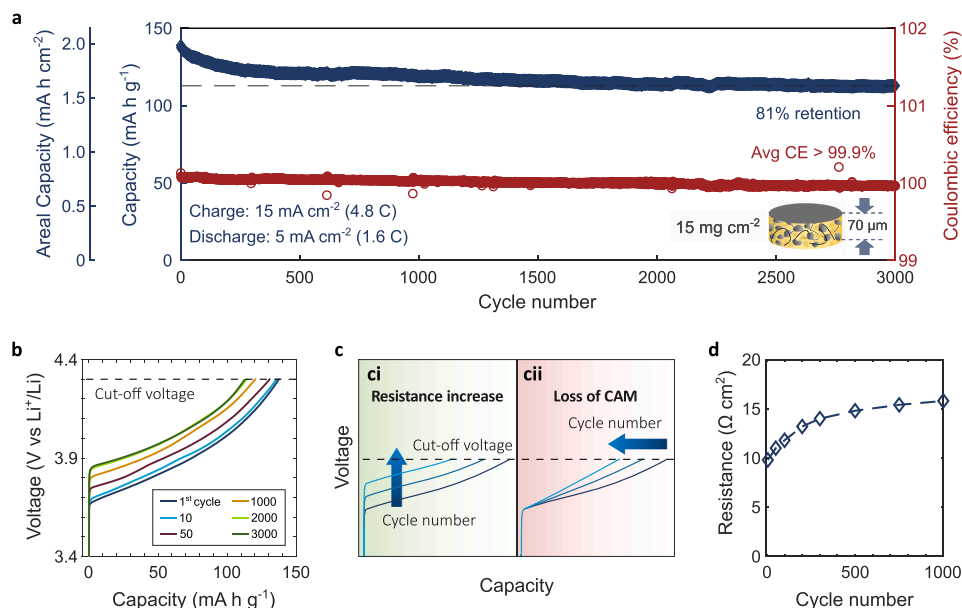


Fig. 2. Fast-charging cycle performance (a) Discharge capacity at 30°C and $15/5 \text{ mA cm}^{-2}$ with cycle number. The cycle life data was obtained in a 2-electrode arrangement, after the cycle profile in Fig. 1c had already been applied. The coulombic efficiencies were averaged neglecting the first cycle. (b) Corresponding charge curve evolution. (c) Schematic of the voltage/capacity charge curve evolution with increasing cycle number assuming galvanostatic cycling caused by (left) an expected increase in resistance at the CAM/SE interface and (right) loss of cathode active material. (d) Interfacial resistance in the composite cathode with cycle number.

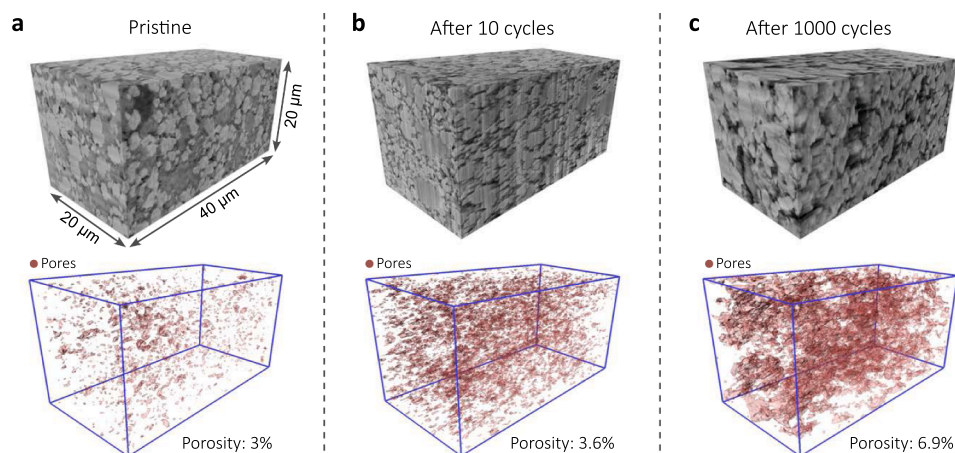


Fig. 3. Evolution of the cathode microstructure and pore volume (a) before cycling, (b) after 10, and (c) after 1000 cycles. 3D reconstructions of the composite cathode SEM microstructure can be found in Videos S1–S3 (available online).

comparatively slow rate of pore volume increase that was ascribed to the strategy of restricting the SOC range to limit CAM volume change to < 3 % [49].

Supplementary material related to this article can be found online at [doi:10.1016/j.addma.2020.101681](https://doi.org/10.1016/j.addma.2020.101681).

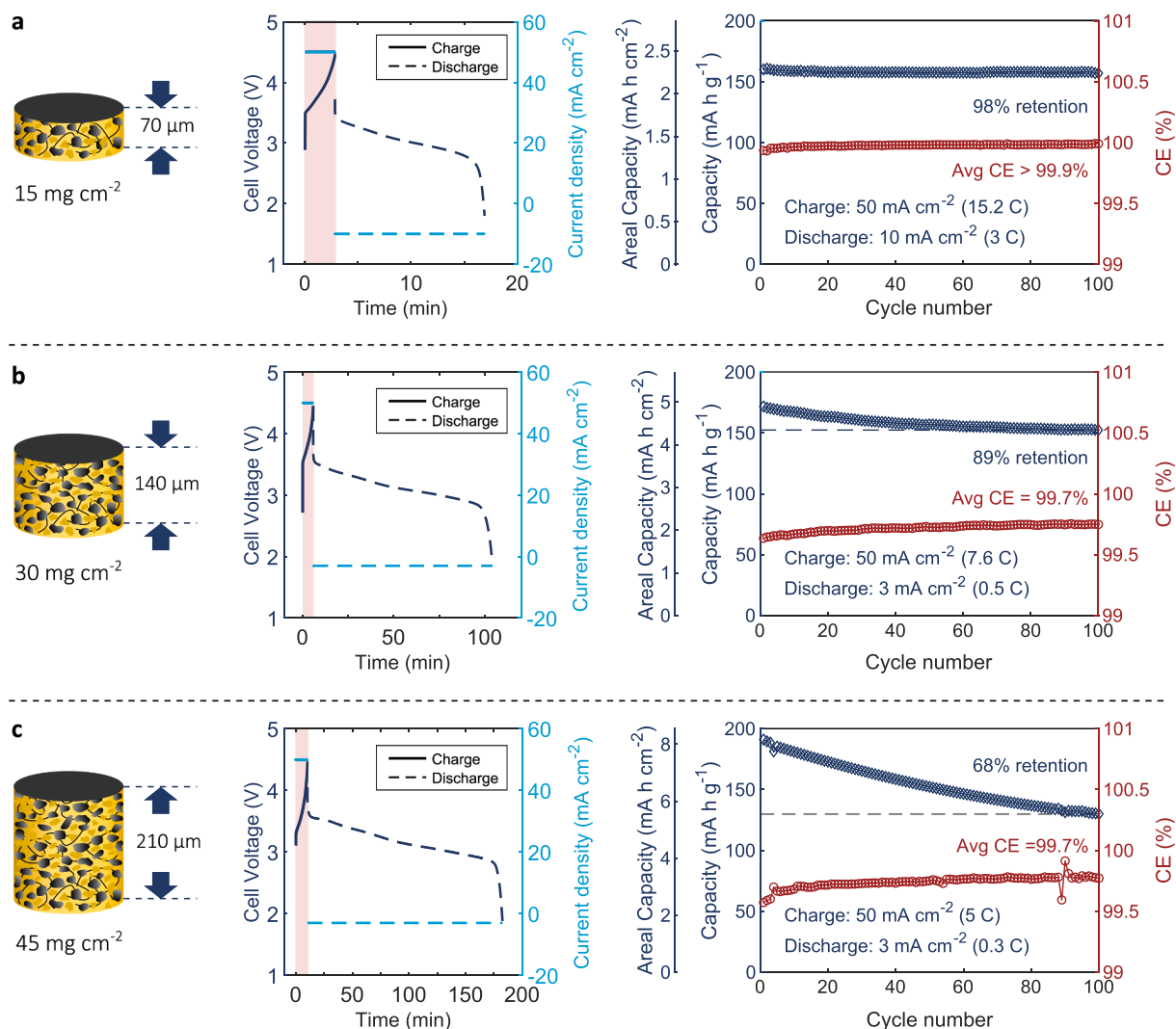


Fig. 4. Exploring increased cathode loadings. Cycle behaviour at a charge current density of 50 mA cm^{-2} and 80°C for different CAM loadings measured in a 2-electrode arrangement. One charge/discharge cycle and the corresponding capacity fade up to 100 cycles (without first cycle) for an active loading and C-rate during charge of (a) 15 mg cm^{-2} , 15.2 C (b) 30 mg cm^{-2} , 7.6 C (c) 45 mg cm^{-2} , 5 C. The cell voltage was measured at the cathode vs. the Li-In anode.

3.4. Exploring increased cathode loadings

Based on the encouraging results above, cathode thicknesses typically used in conventional LIBs, and even higher active loadings, were then investigated in Fig. 4a–c, from 15 mg cm^{-2} ($70 \mu\text{m}$) to 30 mg cm^{-2} ($140 \mu\text{m}$) and 45 mg cm^{-2} ($210 \mu\text{m}$). A current density of 50 mA cm^{-2} was used to keep charging times short, even for the thicker cathodes, and are amongst the very highest charging rates reported for SSB cycling. To maintain CAM utilization $> 70 \%$, the temperature was raised to 80°C , which led to extra capacity of $39 \pm 1.4 \text{ mA h g}^{-1}$ compared with 30°C at a charging current density of 15 mA cm^{-2} (Fig. S12) [41]. The increased temperature successfully facilitated a higher CAM utilization for the same current density (but therefore lower C-rate), as shown in Fig. 4, because of the relatively good ionic and electronic percolation in the composite cathode as previously described. However, the increase in temperature is also expected to increase the rate of any side reactions at the LPSCl/NMC interface. Previous investigations showed that particularly in high oxidative environments, at cell voltages $> 4.2 \text{ V}$, the CAM can react chemically with parts of the electrochemically decomposed products of the sulfide SE [51,52]. Increasing the composite cathode thickness increased the total SE/CAM interfacial area so that at a constant current density, local exchange current densities decreased. This lower local current density reduced the diffusion overpotential in the CAM (which intrinsically limits fast charging) and therefore allowed a higher capacity to be achieved before the cut-off voltage was reached [17].

At 80°C , CAM utilization was 85% after only $\sim 10 \text{ min}$ of charging at a current density of 50 mA cm^{-2} corresponding to an areal capacity of 8 mA h cm^{-2} . The retained cathode capacity at a thickness typically used in a LIB of 15 mg cm^{-2} and $70 \mu\text{m}$ was almost 100% after 100 cycles as shown in Fig. 4a. Even thicker cathodes had a lower cathodic overpotential (at lower effective C-rate), which led to higher effective cut-off voltages, exacerbating sulfide electrochemical instability and CAM volume change, and thus accelerating degradation over 100 cycles (Fig. 4b–c). As mentioned above, the combination of high CAM utilization (higher cell voltage) and higher temperature generally promotes interfacial side reactions and mechanical degradation. Fig. S13 shows the charge/discharge curves corresponding to Fig. 4 with a faster increase in overpotential with cycle number for thicker cathodes. Overall, the cathode performance in Fig. 4 at 50 mA cm^{-2} and a charging time of $< 10 \text{ min}$ represents a significant step forward in the performance of thick SSB cathodes and shows that fast charging can be compatible with unconventionally thick high areal capacity cathodes.

4. Discussion

The excellent cathode charging performance was attributed to two factors. First, the careful combination of materials and process conditions to meet criteria (i) to (ix) given above. For example, a targeted low volume change of $\sim 3 \%$ was confirmed in Fig. S14, which shows the range of Li extracted (y) during asymmetric charge/discharge at $15/1 \text{ mA cm}^{-2}$ translated to a SOC range between 7% ($y \sim 0.17$, discharge) and 79% ($y \sim 0.69$ charge). Second, the 3-electrode set-up, not often used for SSBs, allowed the underlying performance of the cathode to be investigated excluding any overpotential from the Li-In anode [53–55].

NMC with 83% Ni has an approximate volume change of only 3% for a SOC cycling in the range $10\text{--}80 \%$, but nonetheless provides a relatively high capacity of $> 150 \text{ mA h g}^{-1}$. Cycling between $0\text{--}100 \%$ SOC would give more capacity ($\sim 210 \text{ mA h g}^{-1}$) but at the price of a more pulverizing volume change of approximately 6% [31]. Volume changes of individual CAM particles within the composite cathode are expected to be relatively homogeneous throughout the thickness even for the higher loadings investigated herein because the ionic current in a SE is approximately driven by the electric field alone (transference number = 1) and there is no electrolyte concentration overpotential build-up as in a LE [56]. Based on the relatively low capacity fade and

low pulverization of the CAM, it was likely that the CAM particle volume change remained in a relatively benign range $< 3 \%$. Similarly to the excellent cycle life of NMC electrodes in LIBs at 1 C as well as 6 C and 100 cycles, the SC morphology was integral to realizing the relatively low degradation rate [57,58].

Despite the sulfide SE's thermodynamic instability, cathodes can fully function for 3000 cycles at high charge current density. Li-ion and electron percolation were mostly preserved throughout cycling because of the high initial compaction of SE particles and the use of relatively long ($100\text{--}200 \mu\text{m}$) CNFs which likely enabled cycling at relatively low stack pressure [31]. Efficient percolation in the composite cathode is also key to avoid any uneven electrochemical reactions, particularly at high current density that promotes volume expansion in locally preferred CAM particles in non-optimized cathodes.

A comparison of the specific energy of composite cathodes as a function of current density is shown in Fig. 5. For consistency, only pellet-type SSBs of similar thickness and cycled in a similar cell set-up as that used here are included [5,18,20,29,42,44]. Most prior work has been limited to relatively low current densities and/or low areal capacity that led to a low specific energy. These experiments were also conducted in a 2-electrode arrangement without information about the anode overpotential, and it is possible charging during testing was stopped too early. Therefore, some of the prior studies may have underestimated potentially encouraging underlying cathode performance. Nonetheless, the current work shows a marked improvement over previous studies. To give a perspective on the energy density of a future SSB that used the same composite cathode as that investigated here, a Ragone plot is provided in Fig. S15 assuming a Li anode and a thinner SE of $20 \mu\text{m}$ (that might be manufactured by slurry casting for instance) [59]. Fig. S15 shows that these SSBs could deliver a high specific power of $> 1000 \text{ W kg}_{\text{cell}}^{-1}$ while maintaining a high specific energy of $\sim 400 \text{ W h kg}_{\text{cell}}^{-1}$.

All cathodes investigated in this study were prepared without any CAM coating or polymer binder, and the use of the latter, likely required to form more scalable sheet-type cell formats, can be expected to undermine some of the performance data reported here. Our results demonstrate that argyrodite-based composite cathodes designed

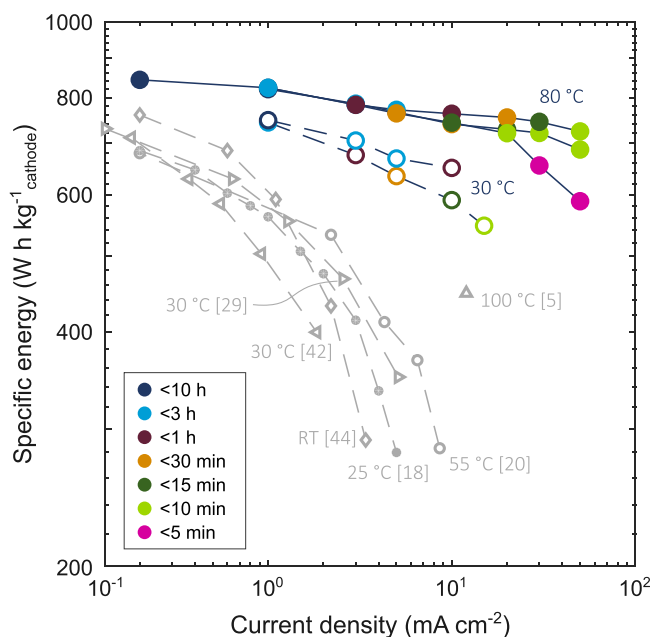


Fig. 5. Comparison of specific energy at different current densities. The specific energies from this study (colours) and the literature (gray) were calculated based on the cathode performance and CAM mass. The different colours indicate the charge time.

according to holistically combined criteria are suitable for fast-charging applications, elevating the SOC from 10 % to 80 % in only 10 min.

5. Conclusions

Design criteria for a fast-charging solid-state cathode with long cycle life were specified and an argyrodite-Li-Ni-Mn-Co oxide-based cathode following these criteria was fabricated. A very high charge current density of 15 mA cm⁻² was retained at a high capacity of 150 mA h g⁻¹ at 30 °C (71 % active material utilization, ~8 min charging time). Cut-off voltages were precisely controlled following charging analysis in a 3-electrode arrangement. Fast charging (4.8 C) was demonstrated for 3000 cycles with 81 % capacity retention. The pore volume in the cathode increased progressively and any active particle isolation played only a small role in capacity fading. A 210 µm thick cathode was charged at 50 mA cm⁻² and a charge time of ~10 min could be sustained at an areal capacity of 8 mA h cm⁻² (85 % active material utilization). This work showed that sulfide-based composite cathodes can operate well at fast-charging rates, especially where electrode preparation provides a high as-manufactured density with dispersed active particles in intimate contact with the solid electrolyte. Applied design strategies can serve as a guideline for the development of fast-charging solid-state cathodes.

CRediT authorship contribution statement

Christopher Doerr: Conceptualization, Data curation, Formal analysis, Methodology, Visualization, Writing – original draft. **Xiangwen Gao:** Formal analysis, Methodology, Validation, Writing – review & editing. **Junfu Bu:** Data curation, Visualization. **Samuel Wheeler:** Methodology, Validation. **Mauro Pasta:** Supervision, Writing – review & editing. **Peter G. Bruce:** Supervision, Writing – review & editing. **Patrick S. Grant:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding was provided by the UK Engineering and Physical Sciences Research Council (EPSRC) and the Faraday Institution through projects SOLBAT (FIRG026) and NEXTRODE (FIRG015 and FIRG066), and The Henry Royce Institute for Advanced Materials (EP/R010145/1). We are grateful to the David Cockayne Centre for Electron Microscopy, Oxford University.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2024.110531](https://doi.org/10.1016/j.nanoen.2024.110531).

Data availability

Data will be made available on request.

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