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ARJUNA: An Electrochemical Interface Mapping Probe for Solid-State Batteries

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Solid-state batteries (SSBs) are promising candidates for next-generation energy storage, although their performance can be compromised by interfacial heterogeneity within the electrolyte. Furthermore, ensuring the quality of large form-factors electrolyte film is crucial for establishing a robust manufacturing platform for solid-state batteries. Herein, we report on the use of ARJUNA, an electrochemical interface mapping system, to characterize heterogeneities at solid electrolyte interfaces and to serve as a quality control system for SSB manufacturing. In addition to spatial mapping, the proposed system can also probe the interface behavior as a function of pressure and temperature. We present the operating principle, design, instrumentation, and evaluation of the system alongside a typical hybrid solid electrolyte produced using two common manufacturing processes. This report showcases the capability of ARJUNA to probe the heterogeneity and quality of processed solid electrolyte films.

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Solid-state batteries have the potential to offer increased energy densities compared to conventional Li-ion batteries by coupling Li metal anode with high voltage cathodes.^{1–3} However, the durability and cyclability of SSBs are hampered by the inherent issues due to SSB architecture.^{4–6} Interfaces are a key driver of performance in solid-state batteries.⁷ Heterogeneities at interfaces within components (intrinsic interfaces) as well as at the interfaces between components (extrinsic interfaces) have been reported to dictate the onset and growth of degradation pathways in solid-state batteries.^{8,9} The nature of the heterogeneities could be linked to surface roughness,⁸ microstructure, phase,^{9,10} resistivity, or kinetics, among other factors. Tracking and quantifying such heterogeneities at the solid | solid interfaces is crucial for the development and commercialization of solid-state batteries, despite being a challenging experimental task.¹¹

Assessment of heterogeneity is an important aspect of quality control of the solid-state battery components.¹² Recent reviews have highlighted the directed multi-scale characterization approaches leveraged to probe the nanoscopic to mesoscopic heterogeneities in solid-state battery interfaces.^{7,13,14} Synchrotron tomography is used extensively to probe meso-scale interfacial heterogeneity.^{9,10,15–19} Apart from tomography, atomic force microscopy is also utilized to probe the heterogeneity in solid electrolytes. Jiang et al. showed the strong discrepancy in ionic and electronic transport in hybrid solid electrolytes is related to the LPS/polymer boundary.²⁰ Wang et al. used electrochemical strain microscopy to probe the differences in ion transport at the surface of NASICON-type $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP). In addition to these experimental studies, numerous theoretical studies have also been conducted.^{21–23}

While the aforementioned techniques offer great insight into the importance of heterogeneities for solid-state battery performance, the key bottleneck is their relative inability to provide form-factors interface information that is at a commercially relevant scale. Typically, tomography measurements are carried out on cells with an interfacial area of $<1 \text{ cm}^2$ while AFM mapping is typically carried out on domains in the range of $\sim 100\text{--}500 \text{ }\mu\text{m}$. In addition to this, coupling the impact of temperature and pressure needs to be probed which is extremely difficult to incorporate in these techniques. In conventional Li-ion batteries, approaches like hyperspectral imaging, X-ray radiography, laser calipers, IR thermography, as well

as optical videography are used to assess the quality of individual cell components. However, detecting the heterogeneities of solid electrolytes such as roughness, impedance, and microstructure may not be functional using such approaches. Electrochemical impedance spectroscopy as well as high voltage pulses are less prevalent but have been proposed as alternate methods for online quality control of battery components. So far, there are no demonstrated solutions for probing the heterogeneity of solid-state battery components that have the potential to be deployed at scale.

Herein, we present a reliable method for mapping solid surface interfaces aimed at characterizing the interfaces of solid-state battery components. The hardware and software control units used in this method are described in the methods section. The mapping system developed here is termed ARJUNA. We evaluate the developed platform by assessing the heterogeneity of hybrid solid electrolytes produced by two different processing methods: drop casting and doctor blading. The results of the mapping study suggest that the doctor-blading approach offers better quality films compared to the drop-casting method. The developed platform can aid in designing and calibrating of highly uniform battery components.

Experimental

Materials processing and characterization.—Appropriate amounts of PEO ($MW_v = 400 \text{ kDa}$; Sigma-Aldrich) and Al-doped LLZO (Ampera) were dispersed in acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) along with LiTFSI (95.99%, Sigma-Aldrich) to achieve an effective 60 wt% for the inorganic component. The PEO:LiTFSI ratio was maintained at 4:1. The dispersion was ball-milled to obtain a uniform suspension. The suspension was then either drop cast on a petri dish or doctor blade coated onto a mylar film and was left to dry overnight. Subsequent testing was carried out on the dried films. SEM micrographs of the dried films were collected on a Zeiss MERLIN FE-SEM. All SEM micrographs were collected at 3 keV electron high tension and a working distance of 8.5 mm.

Mapping setup development.—A spring-loaded probe was developed as shown schematically in Fig. 1. The probe consists of a hollow aluminum sleeve within which a spring with a known spring constant as well as the metallic probe end are loaded. This assembly is mounted on an XYZ gantry to allow for accurate positioning. For this work, we use a Hyrel HR engine's positioning system as the gantry. This gantry provides an X- and Y- resolution of $1.25 \text{ }\mu\text{m}$ and a Z- resolution of $1 \text{ }\mu\text{m}$. The resultant assembly is

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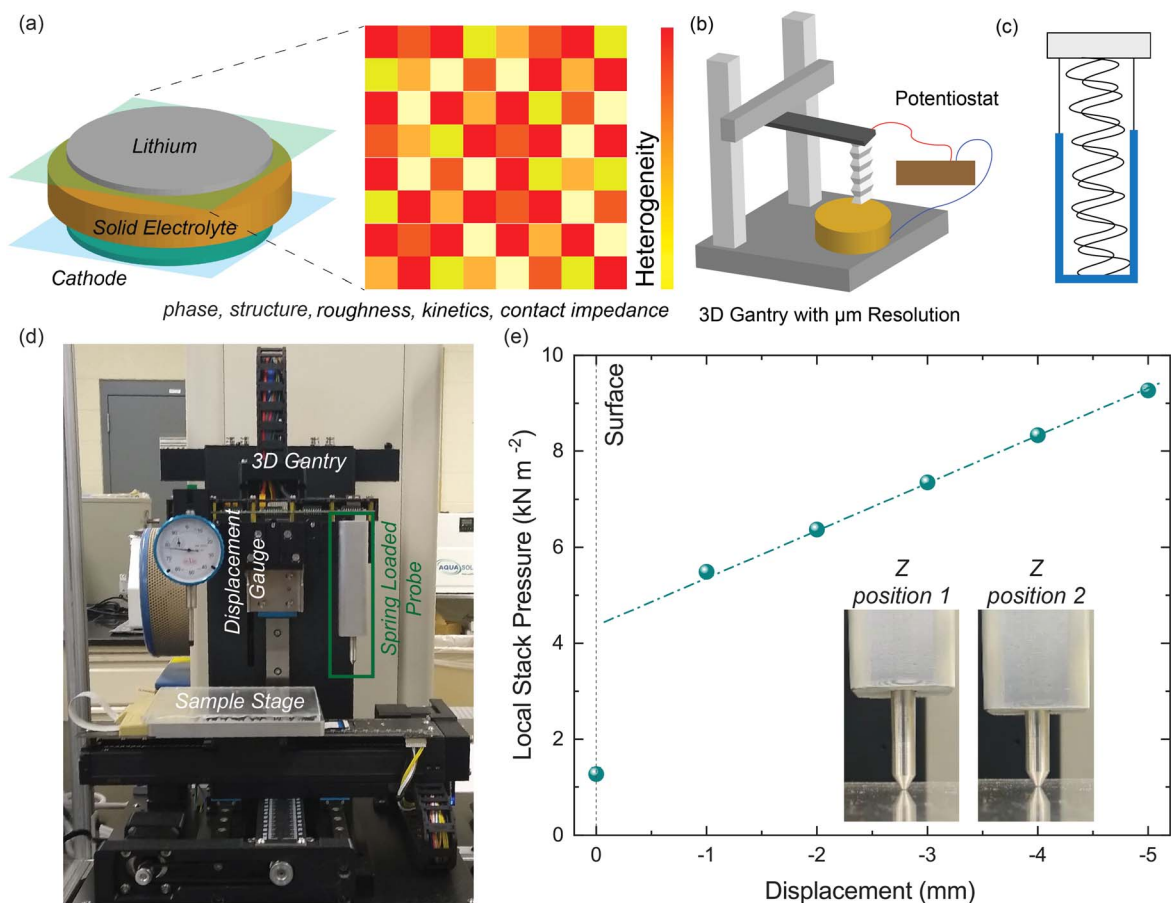


Figure 1. (a) Schematic describing interfacial heterogeneity in solid-state batteries and their potential origins. (b) Schematic diagram of the developed solution and (c) the spring-loaded probe used to assess the surface electrochemical behavior as a function of pressure. (d) Optical image of the developed setup with key components labeled. (e) Pressure-distance calibration curve obtained for the spring-loaded probe. The inset shows the displacement of the probe w.r.t. the surface at different z-positions.

shown in Fig. 1d. For this setup, the X- and Y-axis are in plane with the sample stage and the Z-axis is along the vertical direction. The pressure exerted by the probe due to vertical motion was calibrated using an Omega load gauge. The motion of the probe can be controlled manually or using an automated routine developed within a LabVIEW framework. For electrochemical measurements, leads from the potentiostat are connected to the probe as well as the mounting stage using a double-sided copper tape. Samples are mounted on the stage and the probe is moved till the tip contacts the surface. Subsequently, electrochemical measurements are performed at various (X-, Y) coordinates at distinct pressures. The working and counter electrodes for this experiment were ion blocking copper foils. The spring-loaded probe on the experimental set-up was covered with a copper tape, while the electrolyte film being investigated was stuck on a similar copper foil using silver paint. In this study, we employed a potentiostatic hold of 2 V for 5 min (to ensure cell polarization reached equilibrium) as the measurement technique to demonstrate the applicability of the developed mapping system. It should be noted that while all the experiments reported here are for room temperature measurement, the stage on which the samples are mounted is equipped with a heater enabling assessing these properties as a function of temperature as well.

Results and Discussions

Pressure calibration on the mapping system was initially carried out by a load gauge placed at the bottom of the probe where in vertical motion of the probe was correlated with the measured load on the sensor (Fig. 1e). The resultant behavior is extremely linear for motions up to 5 mm of the probe achieving a local pressure of ~ 9.5

kN m^{-2} at the maximum displacement. The fitting of the linear segment of the evaluated pressure-distance curve of the setup indicated that for a unit displacement of the probe, $\sim 0.95 \text{ kN m}^{-2}$ pressure is exerted on the substrate. Due to the inaccuracy associated with locating the surface of the load gauge precisely using a probe, there is a discrepancy of measured load at zero displacement. The physical motion of the probe can be visualized in the inset of Fig. 1e.

The solid electrolyte films that were prepared by two processing methods are characterized by scanning electron microscopy to understand the distribution of the organic and inorganic phases. The doctor bladed film shows a comparatively thinner membrane compared to the drop-casted membrane (~ 150 vs $\sim 250 \mu\text{m}$). The surface morphology looks completely different for the two systems (Figs. 2a, 2c) with the doctor-bladed film (Fig. 2a) showing a fairly, dense and uniform surface while the drop-casted membrane showed larger surface inhomogeneities as well as the presence of pores. From the cross-sectional images (Figs. 2b, 2d), it appears that there was some degree of phase separation in both films during the drying process. Typically, hybrid electrolytes achieve percolation of the inorganic phase at ~ 12 vol. % and subsequently aggregation is expected in these systems. At the evaluated 60 wt. % fraction of the organic phase, we expected severe aggregation of the inorganic phase. During the drying process, it is likely these large aggregates settle to the bottom of the film due to gravity. Employing such a high fraction was purposely carried out to make differences in the evaluated surface properties more distinguishable.

Subsequently, we investigated the current response of the processed films by applying potentiostatic hold (2 V, 5 min) to the film at different surface locations as well as at different local

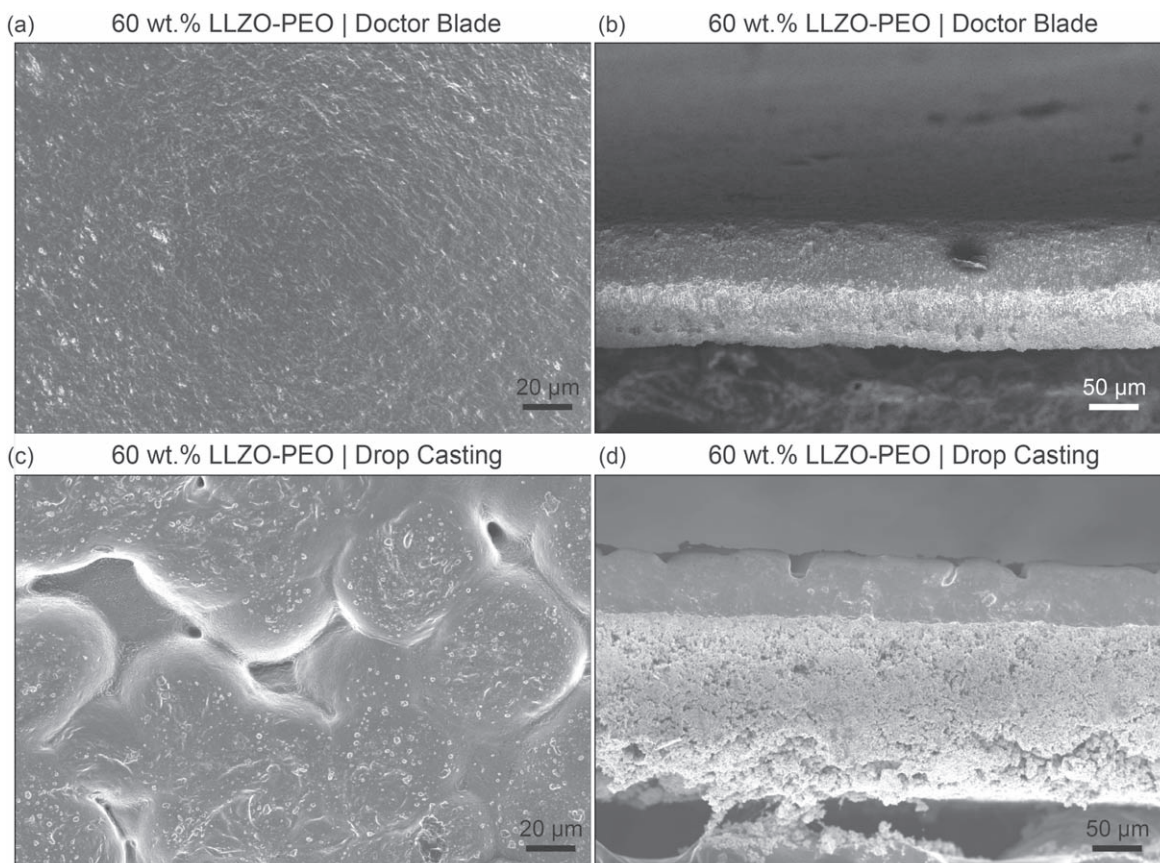


Figure 2. (a) Surface and (b) cross-sectional SEM images of the doctor bladed PEO-LLZO films. (c) Surface and (d) cross-section images of the drop-casted PEO-LLZO films.

pressures (indicated by the Z-height). Typical current decay response profiles for these films are shown in Fig. 3 at a constant potential of 2 V. For the drop-casted film, we observe a monotonic decrease in the current over the measured duration at each surface point over the mapped $15 \times 15 \text{ mm}^2$ area as well as at different local pressures (Fig. 3a). It should be noted that while the initial current values at the beginning of the current hold are different at the evaluated surface points, the steady-state current is identical. Further, carrying out multiple scans at similar locations at different stack pressures yielded similar current decay profiles.

The measurements shown here for different surface locations are at the nominal Z position on the surface of the tested film. Further, as a function of local pressure, the magnitude of that initial current falls monotonically with increasing pressure (Fig. 3b). However, the current decay profiles for the doctor-bladed films are slightly different when evaluated under similar conditions (Fig. 3c). While a similar current decay is observed in the initial part of the potential hold, we observe a slight increase in the current at the latter half of the potentiostatic hold for some of the evaluated surface locations. Also, there is a larger spread in the steady state current observed at different surface locations for the blade-coated film. As a function of pressure, the behavior is more identical to the drop-casted film, albeit with a higher current magnitude. A few observations on the heterogeneities of the film can be made by the collected raw data itself. Both films are highly non-uniform in terms of their local polarization response, this indicates a largely varying internal microstructure as well as ion distributions within the electrolyte composite. We also observed that increasing the local stack pressure, resulted in more uniform and consistent current decay profiles across the measured area indicating a “regularization” behavior with increasing pressure. The influence of pressure on regulating Li metal anode plating and stripping is well established now with

higher pressures favoring stable electrodeposition/dissolution.^{24–27} Our results further suggest that pressure not only can impact anodes, but can also regularize surface transport differences in hybrid solid electrolytes. Whether this behavior would hold in inorganic solid electrolyte materials like garnets and NASICONs is still not clear. However, we can project a similar behavior with softer electrolyte materials like thiophosphates and argyrodites.

It is necessary to understand the origin of the current response and the electrochemical implications of the measurements performed (Fig. 4). The hybrid solid electrolytes investigated here are binary electrolytes containing mobile cations and anions. We can qualitatively assess the response by evaluating the response of the mobile ions when a local bias is applied to the surface. Before applying the bias, it can be assumed that locally the cation and anion charge concentrations are similar. When the bias is applied, in this case, positive bias at the probe tip, anions are driven to the tip. This results in a higher initial current observed in the current response. However, the field-driven ion transport constitutes a local concentration gradient in the electrolyte thereby constituting a transport of the cations in the opposite direction. This leads to a decrease in the current value as time progresses. At a steady state, a constant current is ideally observed when the field-driven and concentration-driven currents balance out. These phenomena are schematically visualized in Figs. 4b and 4c. Drop-casted hybrid electrolytes follow this described behavior in all the observed cases. However, in some locations for the blade coated hybrid electrolytes, an increase in the current is observed at the later stages of the potential hold. This suggests that a net steady state is not achieved between the field and the concentration driven currents and that one of the modes dominate and drives higher currents. Further work is needed to assess the mechanistic origins of this behavior for the developed binary, hybrid electrolytes.

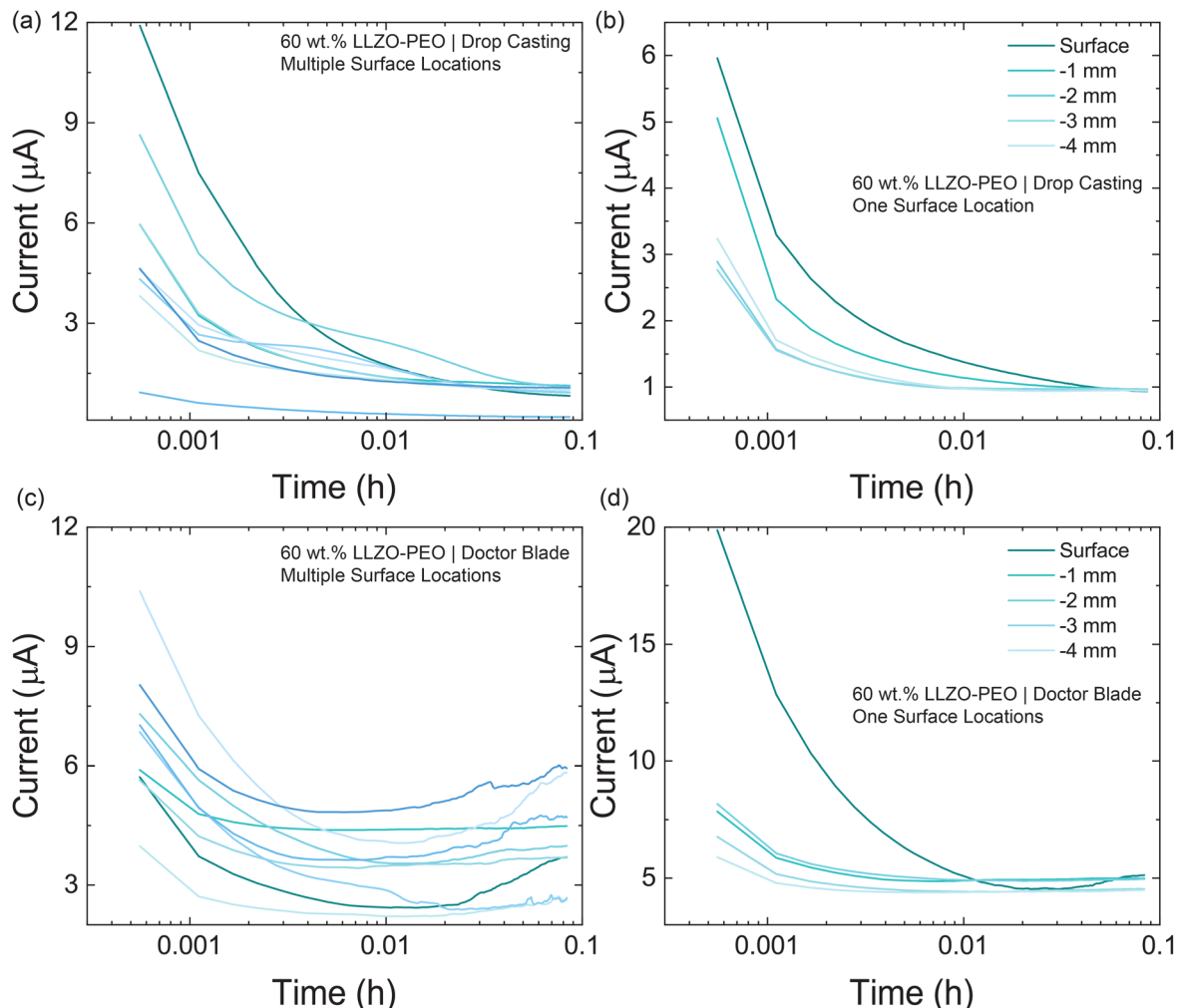


Figure 3. (a) Current response of the drop-casted films at different surface locations at constant local stack pressure and (b) at a single spatial location at different effective local stack pressure. (c) Current response of the doctor bladed films at different surface locations at constant local stack pressure and (d) at a single spatial location at different effective local stack pressure.

To further quantify the transport properties, we evaluate several different strategies for the measured current decay responses. Bruce and Vincent have shown that for binary electrolytes,^{28–30} the ratio of the initial and solid-state currents (i_0 and i_{ss}) is a measure of the transference number of the cation (t^+) as given below:

$$t^+ = \frac{i_{ss}}{i_0} \quad [1]$$

Further, current response (i) of an ideal polarized electrode to a potential step (E) is well established and can be modelled as an RC circuit problem as follows:³¹

$$i = \frac{E}{R_s} e^{-t/R_s C_d} \quad [2]$$

where t is time, R_s is the resistance and C_d is the capacitance. When using this model to fit the current response observed in the hybrid electrolyte systems (Fig. 5), we observe that the exponential decay behavior does not align with the experimental data. This could potentially be due to the non-ideal nature of the electrode/electrolyte interface, wherein there is a possibility of a redox reaction occurring at the copper | hybrid electrolyte interface (Li electrodeposition). In this limit, we also evaluated whether the data could be fit using the Cottrell equation for current response (i) when a potential step to a planar electrode with an electroactive species present at the

interface.³¹

$$i = \frac{nFA D_0^{0.5} C_0^*}{\pi^{0.5} t^{0.5}} \quad [3]$$

where n is the number of electron transfers, F is the Faraday's constant, A is the area of the electrode, D_0 is the diffusion constant, and C_0^* is the initial concentration of the electroactive species, and t is time. Fitting the data with this power-law model shows a better fitting with the experimental dataset.

To assess the heterogeneity of the hybrid solid electrolytes tested, we produced contour surfaces using the parameters obtained from the different fitting methods described above. Figure 6 shows the surface maps of cation transference number as evaluated from Eqn. 1 for the drop-casted and doctor-bladed films at five evaluated local pressure values. Surface heterogeneity in films produced by both the drop-casted as well as doctor-blade processes is highlighted in these contour plots. It is observed that the doctor-bladed film has on average higher effective cation transfer number compared to the drop-casted film. The origin of this could be the difference in microstructures and distribution of the two phases we observe in the drop-casted films compared to the doctor-bladed films from the SEM images in Fig. 2. At higher pressures, we see a small decrease in the measured t^+ value, which is consistent with the decrease in the i_0 value we see in the raw current response (Fig. 3). However, the surface distribution, at least in the case of the doctor-bladed films,

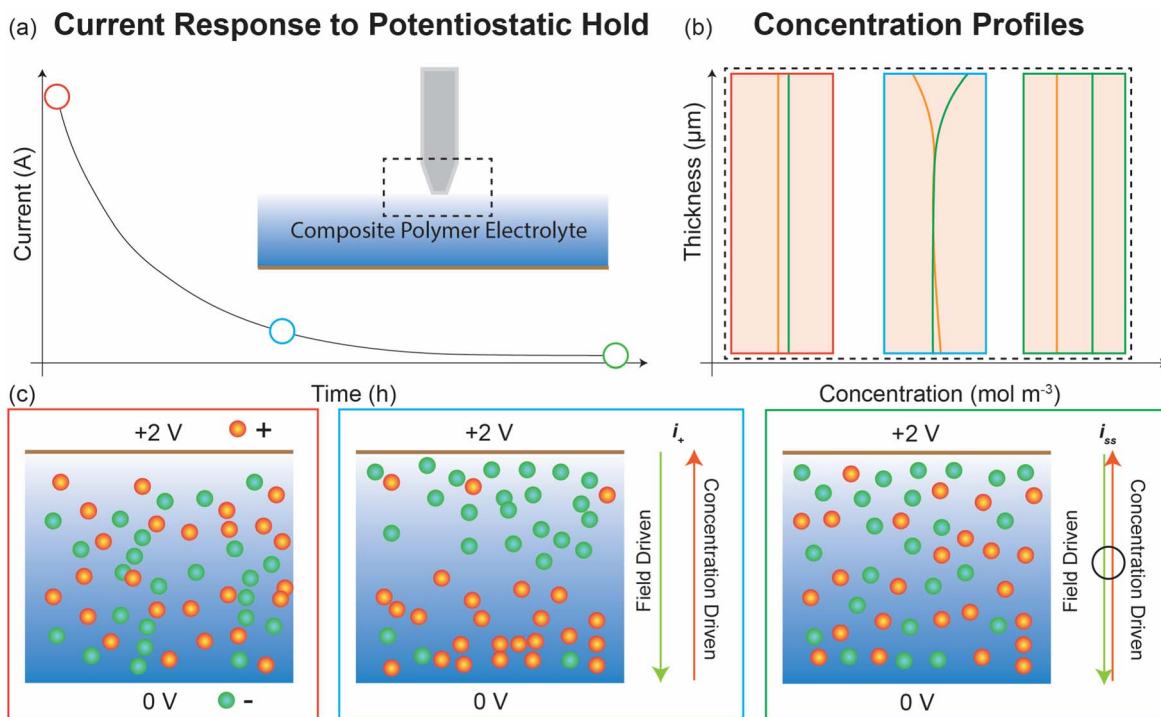


Figure 4. Schematic diagrams describing the (a) current response to the potential hold and the corresponding (b) concentration profiles and the (c) local charge concentration behavior as a function of time.

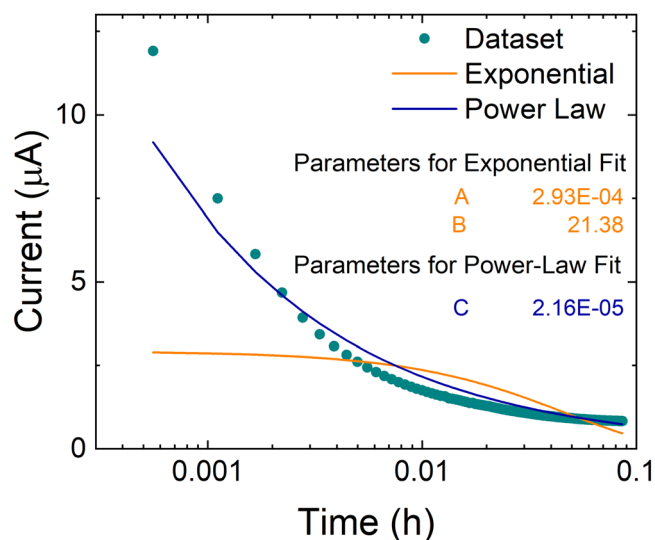


Figure 5. Fitting of the current decay response to an exponential and power law models and the corresponding fitting parameters estimated. The power-law and exponential models are described in Eqs. 2 and 3.

seems to be more homogenous upon increasing local stack pressure (Figs. 6f–6j). For the drop-casted film, we effectively see a mechanical failure of the film at the highest measured pressure resulting in a local shorting that is reflected in a very high evaluated t^+ value (Fig. 6e). It has been seen previously with inorganic solid electrolytes, that domains with lower effective mechanical/transport properties can be the locations of degradation onset during cycling. The mapping tool developed was effective in capturing potentially such a domain on the drop-casted film: a region with potentially poor reinforcement by the inorganic phase that led to the rupture of the film. Similar maps can also be constructed with the fitting constant obtained from the power-law model approximates the diffusion constant of the cation

along with a few lumped parameters. The maps generated with this parameter also showed similar trends and profiles as the t^+ parameter.

There are several underlying challenges and drawbacks of the approach developed here that are important to address. Firstly, the selection of steady-state voltage application and measuring current decay as an analytical method for assessing solid electrolyte films stems from its utility in elucidating ion transport mechanisms. In solid-state electrochemical cells, where convection is absent due to the rigidity of the atomic lattice or the high viscosity of the electrolyte, understanding ion transport becomes crucial. Bruce and Vincent demonstrated that under certain conditions, the ratio of steady-state to initial currents (t^+) provides a valuable approximation of the transference number. Although this method's theoretical underpinnings are derived from ideal electrolytes in simplistic cells, practical utility extends to real electrolytes. Attempts were made to employ electrochemical impedance spectroscopy (EIS); however, the method encountered limitations due to the small contact area of the probe, resulting in inconsistent and high area-specific resistances. Consequently, EIS was deemed unsuitable for our system. Moreover, the use of EIS cannot fully separate the electronic and ionic conductivity even after going through a rigorous fitting procedure. Further, regarding the choice of a blocking electrode as the counter electrode, our experiments were conducted under ambient conditions without the capability to incorporate reactive materials like lithium into the setup. Therefore, the ion blocking electrode (Cu) was chosen for its simplicity and compatibility with our experimental constraints. As for the decoupling of contributions from the working electrode (WE) and counter electrode (CE), our focus primarily lies in understanding ion transport within the electrolyte, directly reflected in the steady-state current response. At this stage, we have not undertaken the deconvolution of WE and CE contributions. In summary, the steady-state voltage application coupled with current decay analysis offers a valuable initial approximation of electrolyte transference numbers, suitable for our experimental setup and conducive to understanding ion transport in solid-state electrochemical cells. Further, this measurement can be easily integrated into on-line quality control systems for

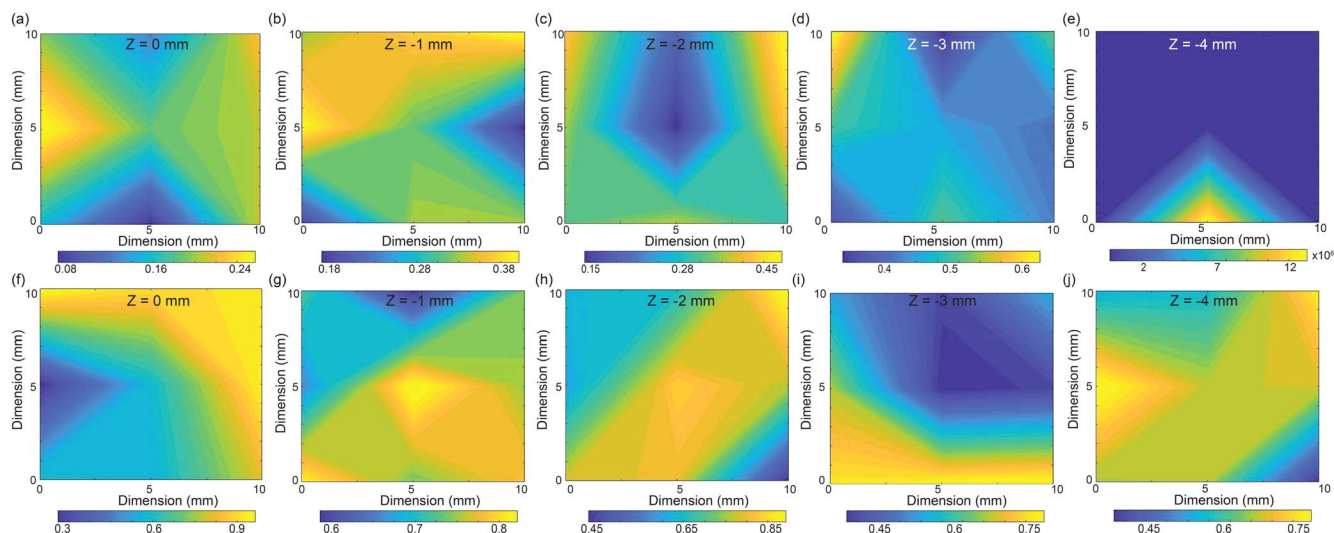


Figure 6. Surface contour plots showing the effective cation transference number estimated from Eq. 1 for drop casted films (a)–(e) and the doctor bladed films (f)–(j) at different effective pressures.

electrolyte production—which is a primary end use of the tool developed here.

Conclusions

We showcased an interface mapping tool to probe the surface heterogeneities of solid electrolytes at the macro-scale coupled with pressure in this report. The developed platform has the potential to be scaled up and integrated into online quality control systems for the high-volume production of solid electrolytes. The quality of the films is assessed using simple electrochemical measurements: in this case a potentiostatic hold with Li-ion-blocking conducting electrodes (Cu). The tool can be further extended to include interlayer coatings on the probe as well as anode and cathode materials to interrogate the respective interactions of the material with solid electrolytes. We evaluate the tool on typical PEO-LLZO hybrid solid electrolytes processed with a drop-casting and a blade coating method. The results suggest that the blade-coating method results in a more homogenous processed film compared to the drop-casted method. Overall, the demonstrated tool has the potential to provide a pathway to probe solid electrolyte films for heterogeneity at scale.

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