

# BATTERIES & SUPERCAPS

## Accepted Article

**Title:** Observation of Interfacial Degradation of Li<sub>6</sub>PS<sub>5</sub>Cl against Lithium Metal and LiCoO<sub>2</sub> via In Situ Electrochemical Raman Microscopy

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# Observation of Interfacial Degradation of $\text{Li}_6\text{PS}_5\text{Cl}$ against Lithium Metal and $\text{LiCoO}_2$ via *In Situ* Electrochemical Raman Microscopy

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**Abstract:** Sulfide-based  $\text{Li}^+$  conducting solid electrolytes, such as argyrodite,  $\text{Li}_6\text{PS}_5\text{Cl}$ , for all solid-state batteries can have comparable ionic conductivities with liquid electrolytes. However, the interface between sulfide containing solid electrolytes and Li metal and Li-ion positive electrodes has been found to be unstable, leading to poor cell performance and cycling. Understanding the evolution of interfacial layer between the electrolyte and both electrodes under *in situ* electrochemistry is of paramount importance for designing stable and long-life solid-state batteries. Here, *in situ* Raman microscopy was used to study the interface between  $\text{Li}_6\text{PS}_5\text{Cl}$  electrolyte and metallic Li and  $\text{LiCoO}_2$ . Under potential control, Raman microscopy identified the appearance of degradation products ( $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_x$  and polysulfides) at the electrode/solid electrolyte interface.

## Introduction

All-solid-state lithium-ion batteries (ASSB), utilizing non-flammable ceramic solid-state electrolytes, are attracting intensive interest due to perceived greater safety over Li-ion batteries containing organic liquid electrolytes.<sup>[1]</sup> Recent research efforts have been driven by sulfide family of solid-state electrolytes that display comparable room temperature  $\text{Li}^+$  ionic conductivities to liquid electrolytes, for example,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  ( $1.2 \times 10^{-2} \text{ S cm}^{-1}$ )<sup>[2]</sup> and  $\text{Li}_6\text{PS}_5\text{Cl}$  (in the range of  $10^{-3}$ - $10^{-2} \text{ S cm}^{-1}$ )<sup>[3]</sup>. However, the cycle-life performance of ASSB reported with sulfide based solid electrolytes are typically limited to less than 100 cycles before substantial capacity fade.<sup>[4]</sup> This is due in part because sulfide solid electrolytes possess a narrow electrochemical stability window.<sup>[5]</sup> Out of the sulphide group of electrolytes, the argyrodite  $\text{Li}_6\text{PS}_5\text{Cl}$ , is attracting particular attention because of it aforementioned high conductivity and good processability. However, it shows interfacial instability towards electrode active materials<sup>[6]</sup>. As a result, the discharge capacities of the cells prepared with  $\text{Li}_6\text{PS}_5\text{Cl}$  electrolyte rapidly decreased to below  $100 \text{ mAh g}^{-1}$  with  $\text{LiCoO}_2$ , below  $50 \text{ mAh g}^{-1}$  with  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  after only 25 cycles. The oxidation products of  $\text{Li}_6\text{PS}_5\text{Cl}$  at the interface with these positive electrode materials have been resolved by XPS (x-ray photoelectron spectroscopy) and were found to be S,  $\text{P}_2\text{S}_x$  ( $x \geq 5$ ), phosphates, LiCl, lithium polysulfides, which were ionically insulating and caused the rapid capacity decay.<sup>[6]</sup>

The interfacial instability between the solid electrolytes and electrodes is one of the limiting factors for the utilisation of ASSB's.<sup>[7]</sup> Application of pressure of ca. 7 MPa upon solid-state cells was further identified to be critical for their performance, as the pressure strongly influences the Li creep behaviour during stripping.<sup>[8]</sup> When the potential of the negative or positive electrode is outside of the electrochemical stability window of the solid electrolyte, the solid electrolyte will decompose and form an interfacial layer. A comprehensive first-principle study revealed<sup>[5]</sup> most solid electrolyte materials have a limited electrochemical window and can be easily degraded in contact with common cathode materials. Thus, the characterisation and understanding of the interface between solid electrolytes and electrodes are very important.

The buried nature of these interfaces presents certain challenges in order to characterise them with traditional surface characterisation techniques, whether *ex situ*, *in situ* or *operando*. Predominantly, *ex situ* characterisation of solid electrolyte/Li metal and solid electrolyte/cathode interfaces have been undertaken. The interface between  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  and  $\text{LiCoO}_2$  was studied after being annealed at different temperatures.<sup>[7b]</sup> Breakdown products such as  $\text{La}_2\text{Zr}_2\text{O}_7$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{LaCoO}_3$  were identified with a combination of synchrotron XRD (X-ray diffraction), XAS (X-ray absorption spectroscopy) and XPS techniques. Co and La were also found to diffuse across the interface.  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  was also found to be unstable with  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  with the formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{LaNiO}_3$ .<sup>[9]</sup> The interfacial resistance at the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{LiCoO}_2$  interface was found to increase with cycling.<sup>[10]</sup> In another study, the degraded  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{LiCoO}_2$  Indium solid-state cells were disassembled and the composite cathode was characterised with XPS.<sup>[11]</sup> It was revealed that  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  was oxidised with the formation of S and  $\text{Li}_2\text{P}_2\text{S}_6$  at the interface. This, together with the formation of Li-depletion zone on the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  at the interface caused the high interfacial resistance and capacity degradation. The interface between argyrodite solid electrolytes  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{LiCoO}_2$ ,  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  cathodes were studied by *ex situ* XPS.<sup>[6]</sup> The degradation products included S,  $\text{Li}_2\text{S}_n$ ,  $\text{P}_2\text{S}_x$ , phosphates and LiCl at the interface between the argyrodite and cathodes after cell cycling.  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) were also found to decompose into  $\text{Li}_3\text{P}$ ,  $\text{Li}_2\text{S}$  and  $\text{LiX}$  with metallic Li deposition by *in situ* XPS<sup>[12]</sup>. This result was consistent with molecular dynamic studies<sup>[13]</sup>. Besides the *in situ* study of the structure of some materials by *in situ* XRD<sup>[14]</sup> and neutron

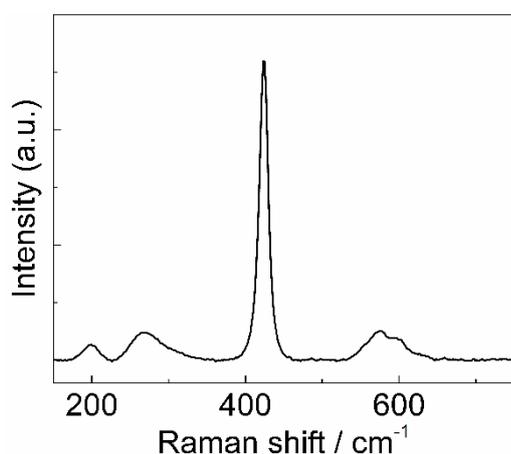
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diffraction technique<sup>[15]</sup>, there are only a handful of *in situ* studies on the solid electrolyte/electrode interface, such as the *in situ* scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) study of the interface between LiCoO<sub>2</sub> and lithium phosphorus oxynitride (LiPON)<sup>[16]</sup> and visualisation of the electric potential distribution at the interface of LiCoO<sub>2</sub> and Li<sub>1-x-y</sub>Al<sub>y</sub>Ti<sub>2-y</sub>Si<sub>x</sub>P<sub>3-x</sub>O<sub>12</sub> using electron holography technique<sup>[17]</sup>.

The ability to do *in situ* observation of the solid electrolyte/electrode interface is paramount for understanding the performance and design interfacial strategies for all solid-state batteries. Raman microscopy is a powerful technique for the detection of structural and chemical information and has been used extensively for studying battery materials<sup>[18]</sup>. However, *in situ* Raman microscopy has not so far being fully explored in the study of solid electrolyte/electrode interface due to challenges of optically accessing solid-solid interfaces. In this study, *in situ* Raman microscopy was implemented to study the interfacial evolution during cycling of Li<sub>6</sub>PS<sub>5</sub>Cl electrolytes with Li metal and LiCoO<sub>2</sub>.

## Results and Discussion

The Raman spectrum of pristine Li<sub>6</sub>PS<sub>5</sub>Cl is shown in **Figure 1**. Peaks at 199, 272, 425, 573, and 600 cm<sup>-1</sup> are all attributed to vibrational modes of PS<sub>4</sub><sup>3-</sup> within Li<sub>6</sub>PS<sub>5</sub>Cl, as shown in **Table 1** and corresponds with previously reported spectra.<sup>[19]</sup> The peak fitting results including the peak centre frequencies/cm<sup>-1</sup> and full width at half maximum (FWHM/cm<sup>-1</sup>) are presented in **Table S1**. The XRD spectra of the powder in **Figure S1** shows the composition is Li<sub>6</sub>PS<sub>5</sub>Cl phase, with a minor Li<sub>2</sub>S impurity. Raman measurements did not detect any Li<sub>2</sub>S on the pristine Li<sub>6</sub>PS<sub>5</sub>Cl powder sample. The ionic conductivity of the Li<sub>6</sub>PS<sub>5</sub>Cl after ball-milling was found to be 1.1 × 10<sup>-3</sup> S cm<sup>-1</sup>, with the impedance spectra and fitting shown in **Figure S2**.



**Figure 1** Raman spectrum of Li<sub>6</sub>PS<sub>5</sub>Cl.

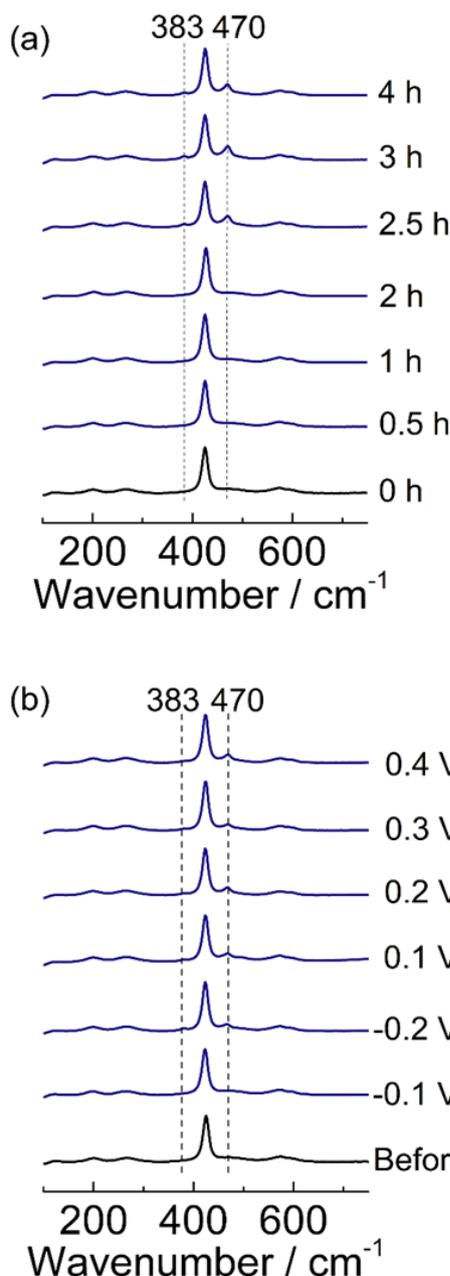
**Table 1** Peak assignments for the pristine Li<sub>6</sub>PS<sub>5</sub>Cl.

Frequency (cm <sup>-1</sup> )	Assignment	Compound	Ref
199	PS <sub>4</sub> <sup>3-</sup>	Li <sub>6</sub> PS <sub>5</sub> Cl	[19]
272	δ <sub>def</sub> (S-P-S) in PS <sub>4</sub> <sup>3-</sup>		[20]
425	ν <sub>s</sub> (PS <sub>4</sub> <sup>3-</sup> ) in PS <sub>4</sub> <sup>3-</sup>		[20]
573	PS <sub>4</sub> <sup>3-</sup>		[19]
600			

Cyclic voltammetry measurements of the solid-state electrolyte Li<sub>6</sub>PS<sub>5</sub>Cl from -0.5 to 7 V vs Li<sup>+</sup>/Li (1<sup>st</sup> cycle) and 8 V vs Li<sup>+</sup>/Li (2<sup>nd</sup> cycle) at 30 °C is shown in **Figure S3**. This result is consistent with the 7 V vs Li<sup>+</sup>/Li stability of Li<sub>6</sub>PS<sub>5</sub>Cl previously reported.<sup>[21]</sup> The Li<sub>6</sub>PS<sub>5</sub>Cl demonstrated stable Li plating and stripping from -0.5 up to 8 V vs Li<sup>+</sup>/Li, although the inset shows instabilities are observed, via current peaks from 2 V vs Li<sup>+</sup>/Li, highlighting the limited electrochemical stability window of this material.

To observe the Li<sub>6</sub>PS<sub>5</sub>Cl interface with metallic Li under potential control, a Li/ Li<sub>6</sub>PS<sub>5</sub>Cl/ Cu cell was assembled within an *in situ* Raman cell and a negative potential was applied between Cu vs. Li. Initially, a constant -0.1 V vs Li was applied at the positive Cu electrode to get continuous Li deposition. The current upon application of the potential was shown in **Figure S4**. As shown in **Figure 2(a)**, after holding the potential for 2 hours, two new peaks at 383 and 470 cm<sup>-1</sup> appear, in addition to the peaks from Li<sub>6</sub>PS<sub>5</sub>Cl. The peak at 383 cm<sup>-1</sup> can be assigned as ν<sub>Li-S</sub><sup>[20]</sup>, from Li<sub>2</sub>S as Li deposition takes place. The peak at 470 cm<sup>-1</sup> can be assigned to the S-S stretching mode of S<sub>2</sub> ions in CuS<sup>[22]</sup>. The formation of CuS likely occurs from the reaction of the Cu current collector with phosphorous sulphides (P<sub>x</sub>S<sub>y</sub><sup>n</sup>). The peak assignments are shown in **Table 2**. In **Figure 2(b)**, a matching cell was applied with a potential of -0.1 V vs Li for 1 hour and -0.2 V vs Li for 1 hour. Again, the same new bands at 383 and 470 cm<sup>-1</sup> also appeared. The potential was then reversed to positive 0.1 V and up to 0.4 V vs Li<sup>+</sup>/Li. The newly formed peaks remained present, highlighting that the CuS and Li<sub>2</sub>S are not removed at these potentials and once formed, remain at the Li/Cu electrode interface. The reduction of Li<sub>6</sub>PS<sub>5</sub>Cl by metallic Li into Li<sub>2</sub>S is consistent with previous reports by XPS results<sup>[12]</sup> and molecular dynamic simulations.<sup>[13]</sup> The fitted Raman peaks (**Table S2**) generally show minor variation in terms of peak position with respect to time or potential, apart from the δ<sub>def</sub>(S-P-S) vibration that is seen to red-shift by ca. 5 cm<sup>-1</sup> from initially position for 272 cm<sup>-1</sup> immediately after potential is applied. The other main Li<sub>6</sub>PS<sub>5</sub>Cl bands do not shift their position, however once potential is applied vibrations associated with PS<sub>4</sub><sup>3-</sup> line shapes broaden significantly, by almost doubling their FWHM. This could be associated with initial decomposition of Li<sub>6</sub>PS<sub>5</sub>Cl once contacted with lithium as the material becomes more amorphous.

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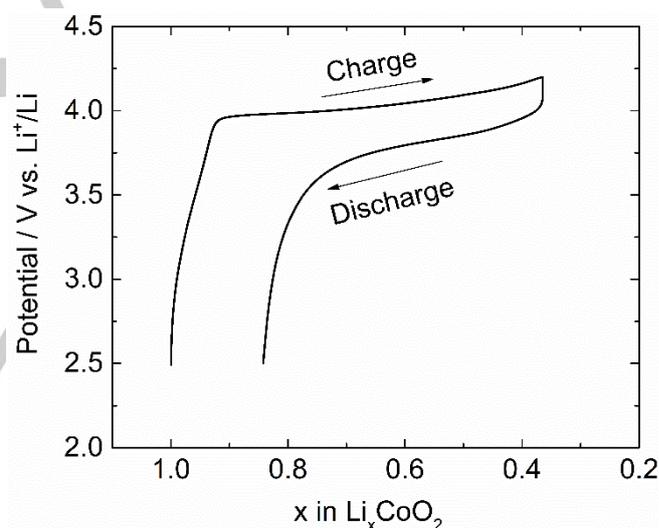


**Figure 2** *In situ* Raman spectra of Li<sub>6</sub>PS<sub>5</sub>Cl/Li interface in Li / Li<sub>6</sub>PS<sub>5</sub>Cl / Cu cell under (a) constant potential of -0.1 V vs. Li<sup>+</sup>/Li; (b) under variable potential.

The stability of Li<sub>6</sub>PS<sub>5</sub>Cl with LiCoO<sub>2</sub> was studied with the *in situ* Raman cell during delithiation and lithiation, as shown in **Figure 3**. The cell exhibited first cycle charge and discharge capacities of 173 and 130 mAh g<sup>-1</sup> respectively. The capacities obtained in the Raman cell mirror those found generally in the literature, thereby demonstrating that representative electrochemical performance can be achieved within the Raman cell. The *in situ* Raman measurements are shown in **Figure 4**. In **Figure 4(a)**, at open circuit potential, 2.38 V, the peak of PS<sub>4</sub><sup>3-</sup> from Li<sub>6</sub>PS<sub>5</sub>Cl at 421 cm<sup>-1</sup> [20] and E<sub>g</sub> and A<sub>1g</sub> of LiCoO<sub>2</sub> at 484 and 593 cm<sup>-1</sup> [23], can be observed respectively. When the cell was charged to 3.97 V, the E<sub>g</sub> and A<sub>1g</sub> peaks decreased in intensity. This is associated with an increase in electronic conductivity from initial Li de-intercalation that reduces the optical skin depth of Li<sub>x</sub>CoO<sub>2</sub> and has been reported in previous investigations of LiCoO<sub>2</sub> using *in*

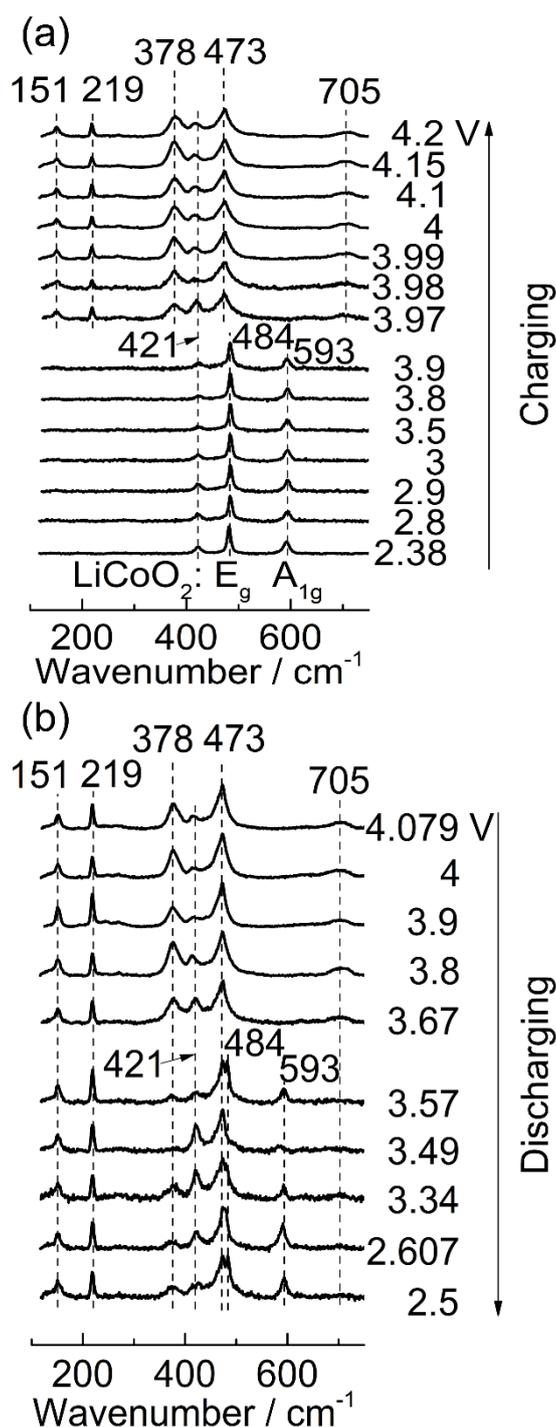
*situ* Raman [23]. At 3.98 V, the E<sub>g</sub> and A<sub>1g</sub> peaks disappear into the background noise, while new peaks appeared at 151, 219 and 473 cm<sup>-1</sup> from S [24], and at 378 and 705 cm<sup>-1</sup> from P<sub>2</sub>S<sub>x</sub> (x = 5 or 6 or 7) [25]. These new peaks remain up to 4.2 V. During discharge in **Figure 4(b)**, the peaks from S and P<sub>2</sub>S<sub>x</sub> remained present down to a potential of 2.5 V. The E<sub>g</sub> and A<sub>1g</sub> bands of LiCoO<sub>2</sub> reappeared from 3.57 V. The formation of S and P<sub>2</sub>S<sub>x</sub> at the interface of Li<sub>6</sub>PS<sub>5</sub>Cl and LiCoO<sub>2</sub> are consistent with previously reported XPS results [6]. The majority of fitted peaks from *in situ* Raman spectra (**Table S3**) showed small variation in terms of peak position/ cm<sup>-1</sup> and full width at half maximum (FWHM/ cm<sup>-1</sup>) that were within experimental error. However, there was peak broadening observed of the most intense band of Li<sub>6</sub>PS<sub>5</sub>Cl at ca. 422 cm<sup>-1</sup> from a FWHM of ca. 20 cm<sup>-1</sup> at 2.8 V to ca. 40 cm<sup>-1</sup> at potentials above 3.9 V. The broadening is reversible as when the potential is lowered below 3.5 V the peak shape narrow returns to FWHM of ca. 20 cm<sup>-1</sup>.

To investigate the longer-term evolution of the Li<sub>6</sub>PS<sub>5</sub>Cl / LiCoO<sub>2</sub> interface a cell was run for 10 charge/discharge cycles and then characterised via *ex situ* Raman after, as shown in **Figure S5**. The formation of S and P<sub>2</sub>S<sub>x</sub> was again detected after cycling, which concurred with the *in situ* Raman measurement.



**Figure 3** Charge and discharge profile for LiCoO<sub>2</sub> / Li<sub>6</sub>PS<sub>5</sub>Cl / Li all solid-state cell measured within the *in situ* Raman cell. During charging, 0.63Li was removed from Li<sub>x</sub>CoO<sub>2</sub>, and 0.48Li was reinserted during discharging, which corresponds to ca. 173 and 130 mAh g<sup>-1</sup> first cycle charge and discharge capacities, respectively.

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**Figure 4** *In situ* Raman spectra of LiCoO<sub>2</sub> / Li<sub>6</sub>PS<sub>5</sub>Cl interface during (a) charging to 4.2 V and (b) discharging to 2.5 V.

**Table 2** Peak assignments for the Li<sub>6</sub>PS<sub>5</sub>Cl interface with Li deposition (Figure 2) and LiCoO<sub>2</sub> under potential control (Figure 4).

Frequency (cm <sup>-1</sup> )	Assignment	Compound	Ref
151	S-S-S bending	S <sub>8</sub>	[24, 26]
219			
272	$\alpha_{\text{def}}(\text{S-P-S})$ in PS <sub>4</sub> <sup>3-</sup>	Li <sub>6</sub> PS <sub>5</sub> Cl	[20]
378	mixed symmetric P-P and P-S stretching modes (A <sub>1g</sub> )	P <sub>2</sub> S <sub>x</sub> (x = 5 or 6 or 7)	[24b, 25a, 25b, 25e, 25g]
383	T <sub>2g</sub> phonon mode in Li <sub>2</sub> S	Li <sub>2</sub> S	[27]
421 - 425	$\nu_3(\text{PS}_4^{3-})$ in PS <sub>4</sub> <sup>3-</sup>	Li <sub>6</sub> PS <sub>5</sub> Cl	[20]
470	S-S stretching mode of S <sub>2</sub> <sup>2-</sup>	CuS	[28]
473	S-S bending	S <sub>8</sub>	[24, 26]
484	O-Co-O bending (E <sub>g</sub> )	LiCoO <sub>2</sub>	[23, 29]
593	O-Co-O stretch (A <sub>1g</sub> )		
573	PS <sub>4</sub> <sup>3-</sup>	Li <sub>6</sub> PS <sub>5</sub> Cl	[19]
600			
705	P-S stretching vibration of terminal S	P <sub>2</sub> S <sub>x</sub> (x = 5 or 6 or 7)	[24b, 25a, 25b, 25e, 25g]

Both *ex situ* and *in situ* Raman analysis highlights the instability of Li<sub>6</sub>PS<sub>5</sub>Cl against both metallic Li or LiCoO<sub>2</sub>. The formation of insulating Li<sub>2</sub>S, S and P<sub>2</sub>S<sub>x</sub> at the interface lead to the increase of interfacial impedance that hampers long-term cycling of ASSBs, as widely observed in the literature. To avoid direct contact to lithium metal or positive electrode materials it is therefore necessary to look to the design of stable Li-ion conducting interlayers. These could be either polymeric or inorganic in nature and then sandwiches between the solid electrolyte and electrode active materials to prevent the formation on insulating side reaction products. Through specific cell design allowing optical access, Raman microscopy can be therefore employed to further understand the complex nature and interplay various buried interfacial regions as they evolve as a function of time, rate of charge/discharge and potential. *In situ* Raman microscopy has been shown to be a useful complimentary tool to study the interface between solid electrolytes and battery electrodes with the capability to deliver both chemical and spatial sensitivity (ca. 1 μm<sup>2</sup>) information, and this will be the focus of ongoing work.

## Conclusion

The interface between Li<sub>6</sub>PS<sub>5</sub>Cl solid electrolyte with metallic Li or LiCoO<sub>2</sub> was studied with both *in situ* and *ex situ* Raman microscopy. Li<sub>2</sub>S formation were detected during lithium deposition with Li<sub>6</sub>PS<sub>5</sub>Cl. Polysulfides, and P<sub>2</sub>S<sub>x</sub> species were detected at Li<sub>6</sub>PS<sub>5</sub>Cl / LiCoO<sub>2</sub> interface during charging. The *in situ* Raman results on Li<sub>6</sub>PS<sub>5</sub>Cl solid-state batteries demonstrate the feasibility of the *in situ* Raman cell set up, in accessing solid/solid interfaces within composite positive electrodes and lithium/solid electrolytes. This method can be translated to other solid electrolytes and present a powerful tool for the understanding the evolution interfaces within solid-state batteries under potential control.

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## Experimental Section

## Materials preparation

Li<sub>6</sub>PS<sub>5</sub>Cl was synthesised by ball milling the mixture of Li<sub>2</sub>S, P<sub>2</sub>S<sub>5</sub> and LiCl, as described by J. Kasemchainan, et al.<sup>[6]</sup>. The materials were handled within an argon glovebox (O<sub>2</sub> < 0.1 ppm, H<sub>2</sub>O < 0.1 ppm). Stoichiometric amounts of Li<sub>2</sub>S, P<sub>2</sub>S<sub>5</sub> and LiCl powders (all from Sigma Aldrich, 99 % purity) were weighed to produce a total mass of 2 g Li<sub>6</sub>PS<sub>5</sub>Cl. The powders were mixed by pestle and mortar for 10 minutes. The airtight zirconia jars (45 ml containing sixteen 10 mm-diameter zirconia balls) were equally filled with the mixture. The high-energy ball-milling process (Fritsch Pulverisette 7) was carried out twice, at a rotation speed of 600 rpm for 7 h. After the initial 7-h of ball-milling the jars were transferred back into the glovebox to loosen stuck powder from the jar wall. The jars were then closed and loaded in the ball mill apparatus for further 7 h. After a total time of 14 h of ball-milling the powder was recovered and ground with pestle and mortar to remove agglomerates.

## Electrochemical Measurements

Cyclic voltammetry to examine the potential stability window of Li<sub>6</sub>PS<sub>5</sub>Cl was measured from -0.5 to 7 V vs Li<sup>+</sup>/Li (1<sup>st</sup> cycle) and 8 V vs Li<sup>+</sup>/Li (2<sup>nd</sup> cycle) at 30 °C in a stainless steel / Li cell within a Swagelok type cell. The scan rate was 10 mV / s. Impedance spectroscopy was performed with a Gamry Interface-1000 device. Li foil was pressed onto the solid electrolyte pellet on both sides with a clamping pressure of 7 MPa. The voltage amplitude was 10 mV. The frequency range was from 1 MHz to 0.2 Hz. The impedance spectrum was fitted with ZView software.

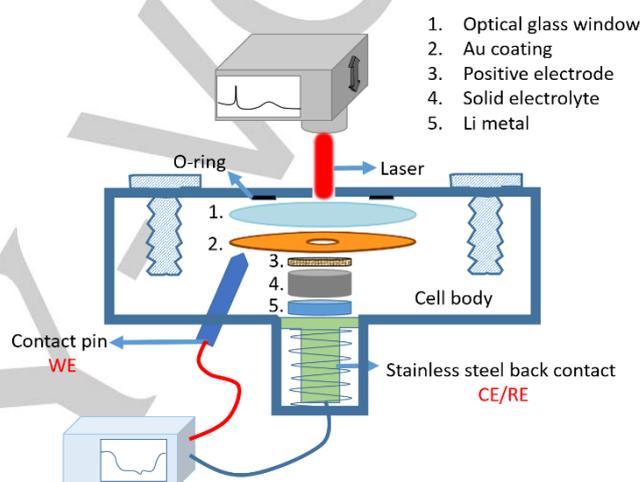
## Raman microscopy

*Ex situ* and *in situ* Raman measurements were collected using a Raman microscope (Renishaw, in via Reflex coupled with an inverted Leica microscope), with a 633 nm laser as excitation source (power < 300 μW), focussed onto the sample using a x50 objective (Olympus). The collected Raman spectra were baseline corrected and peaks fitted using a combined Lorentzian and Gaussian function. Spectral measurement time was 2 seconds with 30 accumulations to ensure good signal to noise ratio to resolve peaks. To check for potential laser damage, Li<sub>6</sub>PS<sub>5</sub>Cl was measured with varying laser intensities and exposure times (Figure S6). No changes in the spectra were observed.

For the assembly of the solid-state *in situ* Raman cell, the solid electrolyte was prepared via (diameter: 5mm) loading into a die and levelled by means of a cylindrical plunger (< 5 MPa), then the mixture of solid electrolyte, LiCoO<sub>2</sub> and carbon black (55:40:5 in weight ratio) was ground in a pestle and mortar for 30 minutes and spread uniformly onto the solid electrolyte pellet and pressed at 360 MPa for 5 minutes. 25 mg argyrodite was used as a separator layer between the positive and negative electrode for one pellet. The total amount of the cathode composite was 3.5 mg. The active material loading was 7.1 mgLiCoO<sub>2</sub>/cm<sup>2</sup> (~1 mAh/cm<sup>2</sup>). A polished lithium metal disk (diameter: 5 mm, Sigma Aldrich) was subsequently pressed onto the other side of the solid electrolyte and sealed in the airtight optical Raman test EL-cell (ECC-Opto-Std). All these handling was performed within an argon containing glovebox.

For the lithium stability measurements, 50 nm of Cu was deposited onto the borosilicate glass window at room temperature within the Moorfield Minilab 080 chamber and used as the current collector for lithium plating. The deposition thickness was controlled by the Inficon SQC-310C deposition controller. For the LiCoO<sub>2</sub> stability test, 50 nm of Au was deposited onto the glass window with a transparent round area in the middle within the Univex 300 chamber. The deposition thickness was controlled by a Maxtek thickness monitor (TM-400). The diameter of the round area was 3 mm. A schematic of the *in situ* Raman cell set up is displayed in Figure 5. A pressure of 0.75 MPa was applied onto the solid-

state battery via the spring on the back contact with the metallic lithium to ensure good contact within the solid state cell and also with the contact pin. For the *in situ* Raman measurement, a potential or current can be applied between the Au / Cu layer at room temperature via a potentiostat (Biologic). The cell was charged and discharged at a rate of 0.1 C for the LiCoO<sub>2</sub> stability study. As the LiCoO<sub>2</sub> was pressed together with the solid electrolyte, the charge and discharge capacities were calculated based on the nominal weight of the active materials for each pellet. For the *in situ* Raman measurement of the LiCoO<sub>2</sub> / Li<sub>6</sub>PS<sub>5</sub>Cl / Li all solid state cell, the laser was focused directly onto the composite positive electrode through a 3 mm diameter transparent round area in the glass without the Au coating (similar to a holed configuration), as shown schematically in Figure 5. For the *ex situ* Raman measurement, the sample was sealed in a hermetically sealed *ex situ* measurement cell with an optical glass window within the glovebox.



**Figure 5** Schematic of the *in situ* Raman cell set up. WE: working electrode, CE/RE: counter electrode / reference electrode.

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**Keywords:** electrode-solid electrolyte interface • electrochemistry • *in situ* Raman • interfaces • Raman spectroscopy

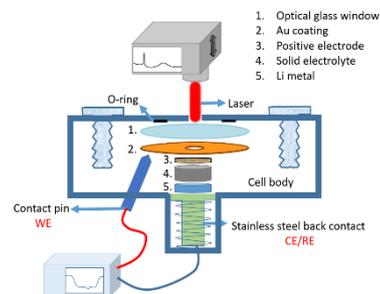
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## Entry for the Table of Contents

*In situ* solid electrolyte - electrode interface

*In situ* Raman microscopy studied the interfacial evolution between  $\text{Li}_6\text{PS}_5\text{Cl}$  and Li metal and  $\text{LiCoO}_2$  during charge and discharge processes.

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