DEVELOPING ELECTROLYTE-CATHODE INTERFACES IN LI-BASED CELLS

Improving the chemical purity and interfacial resistance of solid-solid interfaces

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ABSTRACT

This project investigated the electrolyte-cathode interface for solid-state batteries (SSBs). Li-garnet electrolyte $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (Ta-LLZO) and cathode material $LiCoO_2$ (LCO) were chosen; Ta-LLZO for its high ionic conductivity and wide electrochemical stability[1] and LCO for its chemical stability[2]. Using Raman and SEM data, it was determined sintering at 700 °C for 1 hr in oxygen atmosphere was optimum. Symmetric cells were then fabricated (Fig. 1), with cell #1 showing the lowest interfacial impedance while for cells #2 and #3 the LCO precursor solution used in the mixture formed secondary phases with low conductivity after heating, resulting in high impedance.

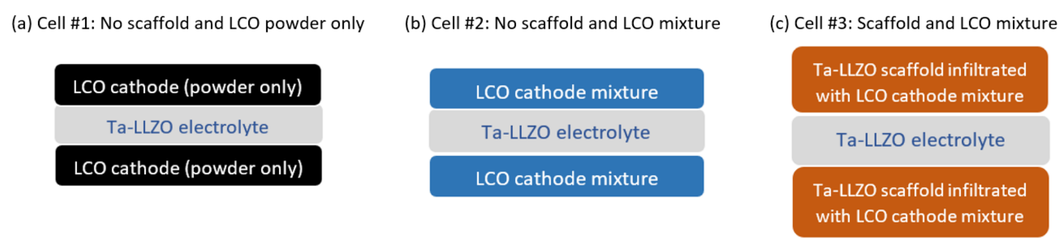

Fig. 1 Schematic of symmetric cells constructed.

METHODS

Section 1: Optimization of sintering conditions

- Ta-LLZO/LCO mixtures were prepared by ball milling commercial Ta-LLZO and LCO powders in a 50-50 wt%. ratio. These were pressed into pellets and sintered at:
  - 700 °C, 800 °C and 900 °C for 1 hr in air.
  - 700 °C for 1 hr in air and oxygen.

Section 2: Symmetric cells

- A film of LCO (1 mg/cm^2) was deposited onto flat, (cells #1, 2) tape-cast Ta-LLZO and LCO solution mixture was infiltrated in Ta-LLZO scaffold (cell #3)(Fig. 1).
  - The LCO solution mixture (cells #2, 3) consisted of a 50-50 wt%. ratio of LCO powder and LCO precursor solution[2] (prepared with $LiNO_3$ and $Co(NO_3)_2{\cdot}6H_2O$).
- Cells were heated at 700 °C for 1 hr in oxygen and coated on both sides with Ag paste.
- Electrochemical Impedance Spectroscopy (EIS) measurements were taken at room temperature.

MOTIVATION

The nonflammability of solid electrolytes in SSBs renders them safer alternatives to conventional Li-ion batteries that utilise liquid electrolytes. The high electrochemical compatibility of Li anodes with LLZO electrolytes further allows for higher capacities compared to traditional graphite anodes[1]. However, a major barrier in advancing SSBs is the electrolyte-cathode interface which exhibits the highest impedance[3], resulting in the need of more research in this area. After optimising sintering conditions, this project explored using a cathode solution mixture containing LCO powder and a LCO precursor solution for in situ synthesis of LCO[2], and the use of a porous scaffold for solution infiltration. This scaffold of the same material as the electrolyte layer has pores that are filled with electrode material and increase the electrolyte-cathode interface while giving support for thinner electrolyte layers.

SECTION 1. OPTIMISING SINTERING CONDITIONS

Sintering temperatures

- SEM images shows higher temperatures improved interfacial contact (Fig. 2).
- However, at higher temperatures insulating secondary phases formed; at 800°C and 900 °C peaks for $LaCoO_3$are seen (Fig. 3).
- So, 700°C was used for both good interfacial contact and to maintain chemical stability.

Sintering atmosphere

- Fig. 4 shows little difference between sintering in oxygen and air at 700°C.
- Nevertheless, an oxygen environment was chosen as research shows CO_2 and H_2O in the air during heating leads to secondary phases, while oxygen ensures chemical stability and low interfacial resistance[4].

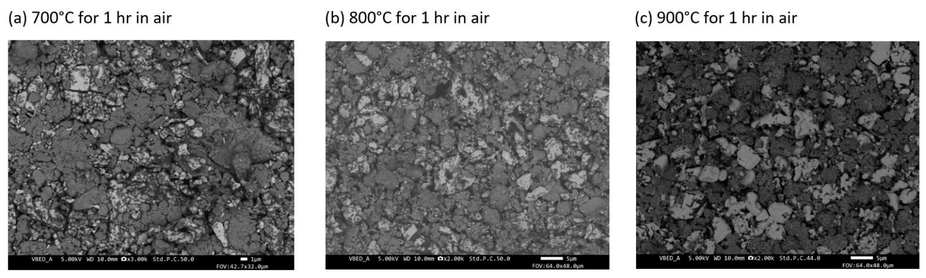

Fig. 2 SEM images of Ta-LLZO/LCO mixtures sintered in air at **(a)** 700°C. **(b)** 800°C. **(c)** 900°C

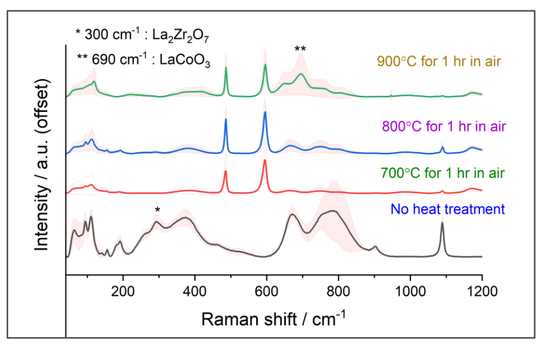

Fig. 3 Raman spectra of Ta-LLZO/LCO mixtures sintered at 700°C, 800°C, 900°C for 1 hr in air, and no heat

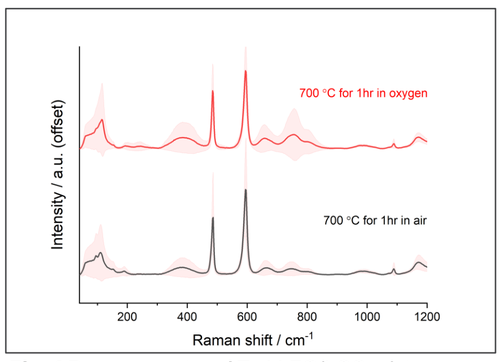

Fig. 4 Raman spectra of Ta-LLZO/LCO mixtures sintered at 700°C for 1 hr in air and oxygen.

SECTION 2. SYMMETRIC CELLS

- Cell #1 had the lowest interfacial impedance (~427 Ω cm^2) while #2, 3 had drastically higher impedances (Fig. 5). The interfacial impedance was calculated from the high-intercept of the second arc (Fig. 6) for cell #1, but fittings could not be done for cells #2, 3.
- From SEM images (Fig. 7), cell #1 forms good interfacial contact, but it is not clear from SEM images alone why cells #2 and 3 (Fig. 8) exhibit high impedance.

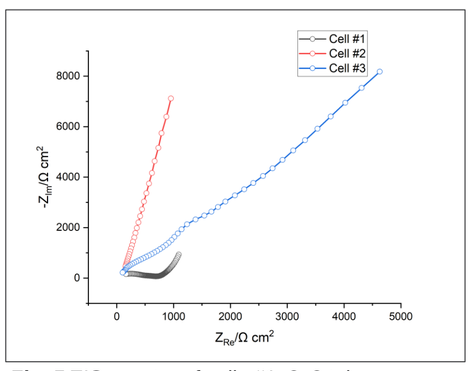

Fig. 5 EIS spectra of cells #1, 2, 3 taken at room temperature.

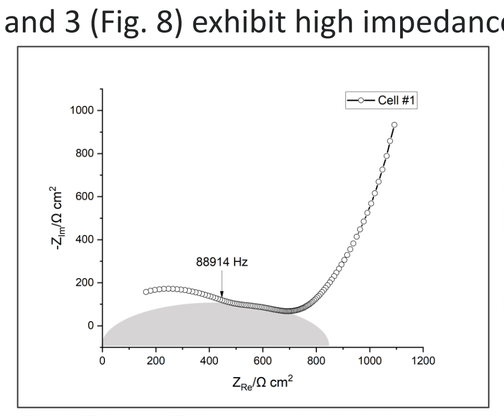

Fig. 6 Enlarged EIS spectra of cell #1 with impedance extraction.

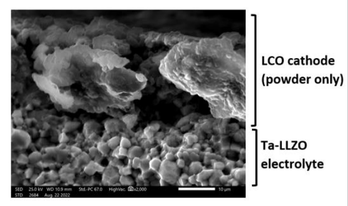

Fig. 7 SEM image of cell #1 .

- EDX and Raman data show that the high impedance of cells #2 ,3 (Fig. 8 and Fig. 9) is a result of the formation of multiple Li deficient secondary phases ($La_2Zr_2O_7$, $LaCoO_3$) and Li_2CO_3 during the sintering process as no excess $LiNO_3$was used. For cell #3 there was also low material loading.

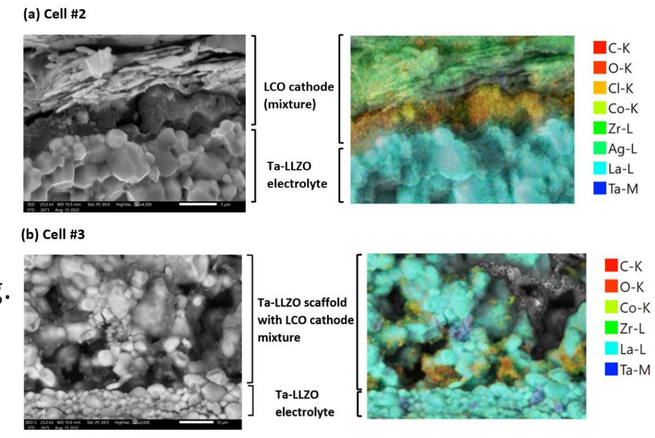

Fig. 8 SEM/EDX images of cells **(a)** #2**. (b)** #3. .

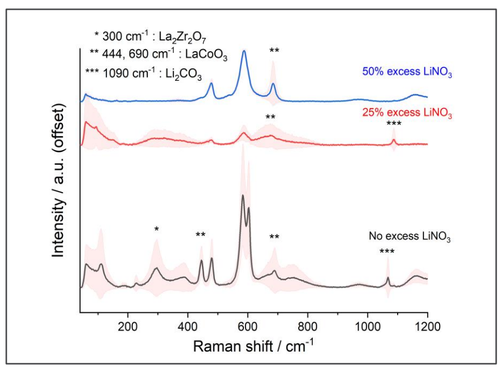

Fig. 9 Raman spectra of Ta-LLZO/LCO precursor solution .

- In order to mitigate this, mixtures of a 50-50 wt%. ratio of Ta-LLZO and LCO precursor solution were heated at 700 °C for 1 hr in oxygen with 25%/50% excess $LiNO_3$ to compensate for Li loss. 25% excess also had Li_2CO_3 formation, but overall, both resulted in none but $LaCoO_3$ (Fig. 9).

CONCLUSIONS

- The optimum sintering conditions is at 700°C for 1 hr in oxygen.
- Using the LCO solution mixture (cells #2,3) resulted in higher impedance than pure LCO (#1) due to secondary phase formation and low loading of LCO in the scaffolds.
- Secondary phase formation can be reduced by accounting for Li loss.

NEXT STEPS

- Using a LCO precursor solution with excess $LiNO_3$ to reduce the secondary phases formed and improve interfacial impedance.
- Using more concentrated LCO precursor solutions to improve in situ LCO synthesis and loading of scaffold loading.
- Construct a full cell with a Li anode to measure charge and discharge characteristics.

REFERENCES

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INTERN BIO

Keziah is studying for a BSc Chemistry at Imperial College London and will be entering her final year. She is an aspiring researcher interested in a wide range of fields spanning from chemical biology to sustainable energy.

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