

Supporting Information

Insight into the Failure Mechanism in Large-scale 18650 Lithium-Sulphur Cell

Surasak Kaenket, Salatan Duangdangchote, Kan Homlamai, Nattanon Joraleechanchai, Titipum Sangsanit, Worapol Tejangkura, and Montree Sawangphruk*

Centre of Excellence for Energy Storage Technology (CEST), Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand.

Experimental

Preparation of LSBs cathode, cell assemble and electrochemical evaluation

The carbon was used as a host of sulphur. The mixture of, sulphur, carbon black (Super P) and CMC binder in a weight ratio of 7:2:1, respectively, was mixed in water forming the 10% of mixed solid content in slurry. The slurry was coated on the Aluminium foil by roll to roll-coating and drying at 60 °C for 24 h. The LSBs were prepared in the argon-filled gloved with cylindrical cell 18650. To compare with CMC binder, co-binder CMC-SBR was prepared. The ratio of carbon black (Super P), CMC, and SBR binder in a weight ratio of 7:2:0.5:0.5, respectively. The cells were assembled in dry room at -40 °C dew point.

The proper amount of the electrolyte is precisely 5 g of 1.0 M Lithium bis(trifluoromethanesulfonyl)imide (LITFSI) with 0.1 M of LiNO_3 in DOL/DME (1:1, v/v) was filled into the cell in which the lithium metal and Celgard 2400 were used as an anode and a separator, respectively. The electrolyte injection was carried out in the Ar-filled glove box using an electrolyte filling machine. Once the electrolyte is added, we allow the cell to rest for 15 min. This resting or 'soaking' period ensures the electrolyte thoroughly saturates both the electrode materials and the separator. After soaking, we placed the battery cell into a vacuum chamber. This vacuum step is designed to help the electrolyte permeate fully into the cell components. Once this is completed, we proceed with the case sealing process. After the cell was sealed, we then wet the cell for 24 h to achieve the adequate electrolyte permeable to the electrode and separator. Note, the same type of electrode, separator, and electrolyte was used in coin cell fabrication. The electrolyte injection was carried out in the ratio of $E/S = 20$.

The NEWARE battery tester was used to evaluate the electrochemical performance of as fabricated LSBs by using the Galvanostatic charge-discharge technique (GCD) at different C-rate ($1C = 1,675 \text{ mAh g}^{-1}$) in a voltage range of 1.6–3.0 V the Metrohm AUTOLAB potentiostat (PGSTAT 302 N) operating NOVA software (1.10) carried out the electrochemical impedance spectroscopy (EIS) of as fabricated LSBs in the frequency range of 1 MHz–100 mHz with an AC potential amplitude of 5 mV.

SEM image and optical microscope image analysis

SEM images of the cathode were captured before cell fabrication using the as-prepared electrode sample, providing insights into the material's morphology, coating thickness, and sulphur element composition, as depicted in figure 1. These SEM images were obtained from the pressed electrodes following the calendaring process, specifically from the centre of the electrode sheet. Throughout the manufacturing process, we closely monitored the thickness and uniformity of the electrode sheet to maintain our quality standards. This meticulous monitoring ensured a representative view of the electrode's microstructure. Due to the constant measurement of the sheet's thickness and uniformity, there should be minimal spatial variation, making the centre a suitable point for general inspection.

After conducting the GCD measurement, the cell was disassembled, and its components, i.e., cathode, anode, and separator, were analysed using an optical microscope. Samples were taken from the middle of the length and width of the electrode and separator within the glove box. It was observed that corrosion occurred severely from the inner roll to the outer roll, with the outermost roll experiencing minimal corrosion.

Furthermore, the SEM images of the cathode after GCD were also investigated. These images were taken from three positions along the roll, i.e., the inner roll, middle roll, and outer roll, at specific locations: 1 cm, 23 cm, and 45 cm from the total cathode length of 47 cm.

Supporting results and discussion

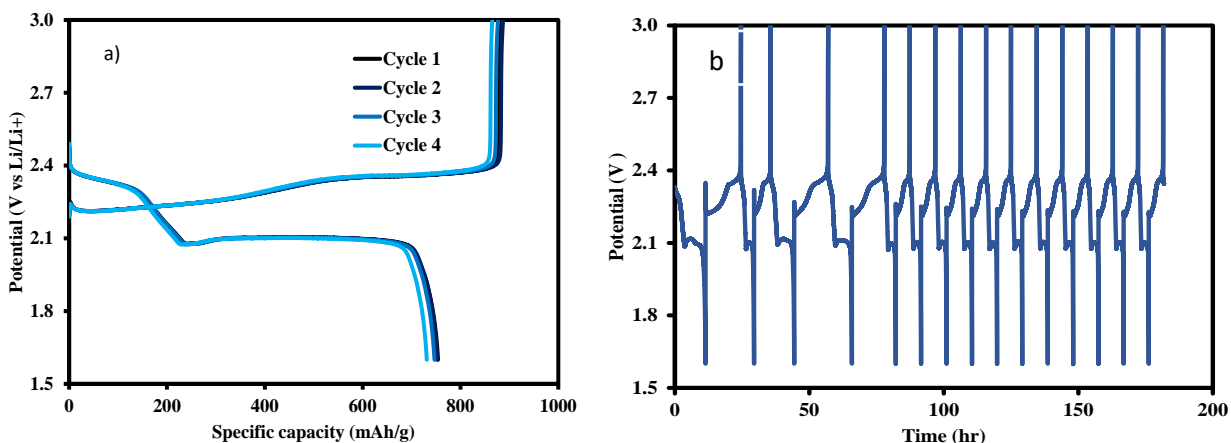


Fig. S1 Coin cell with co-binder CMC:SBR illustrates a) normal discharge profile and discharge plateau contribution at 1C and b) charge/discharge profile at 0.1C at first 4 cycles and 1C at latter cycles.

To compare with the 18650 cell, coin cells using the same type of electrode were also fabricated. The coin cell exhibited a normal discharge profile and demonstrated greater stability than the cylindrical cell, as shown in Fig. S1a and Fig S1b.

Disassembly of the 18650 cell was conducted to investigate its internal components. It was observed that the electrolyte solution turned dark in colour and became thicker, as shown in Fig. S2a. The electrode after cycling showed signs of corrosion and rough surfaces, with yellow and black residue, which might have resulted from the accumulation of poly lithium sulphide. In Fig. S3, a comparison was made between the fresh electrode and separator with their counterparts after cycling. The cathode showed a rough and corroded surface in Fig. S3a.



Fig. S2 Cell disassemble illustrating the electrolyte residue leakage during disassemble (a), cell roll and electrolyte residue out of the case (b), and the electrode surfaces (c).

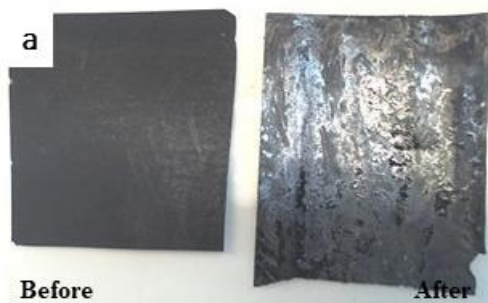


Fig. S3 Cell disassemble before and after cell cycling of (a) sulphur cathode (b) PE/PP/PE separator and (c) lithium metal anode.

The separator underwent a noticeable colour change, transitioning from white to yellow-orange, and displayed dark areas (Fig. S3b). This change suggests the generation of poly lithium sulphide from the cathode, which might have penetrated and accumulated at the separator. The dark areas in the separator originated from the anode side, where the lithium anode reacted with poly lithium sulphide in the electrolyte.

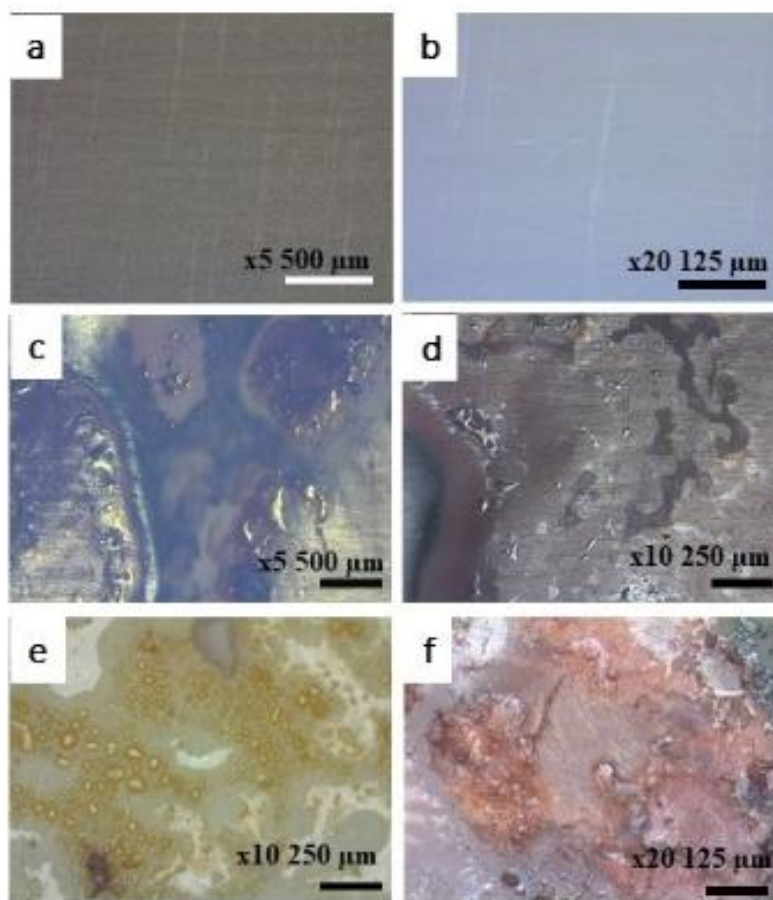


Fig. S4 Optical microscope images of PE/PP/PE separator surface before cycling (a, b), anode side PE/PP/PE separator surface after cycling (c, d), and cathode side PE/PP/PE separator surface after cycling (e, f).

Fig. S4 illustrates the PE/PP/PE separator in LSBs. Before cycling we can observe the clear surface of the separator under microscope in different magnifications (Fig. S4 a,b). After galvanic charge discharge evaluation, the separator showed a wet and rough surface. The separator was wet and its color changed from white to yellow to orange as indicated in Fig. S3b and Fig. S4c-d. On the cathode side of the separator (Fig. S4e-f), it tended to get a darker color from the lithium anode reaction. It might be from the lithium dendrite and a consequence short circuit. While on the cathode side, the separator turned to yellow and orange. This may occur from the color of polysulfide produced from the cathode. The electrolyte solution turned from a colorless solution to dark yellow to black. This indicates the reaction in the electrolyte.

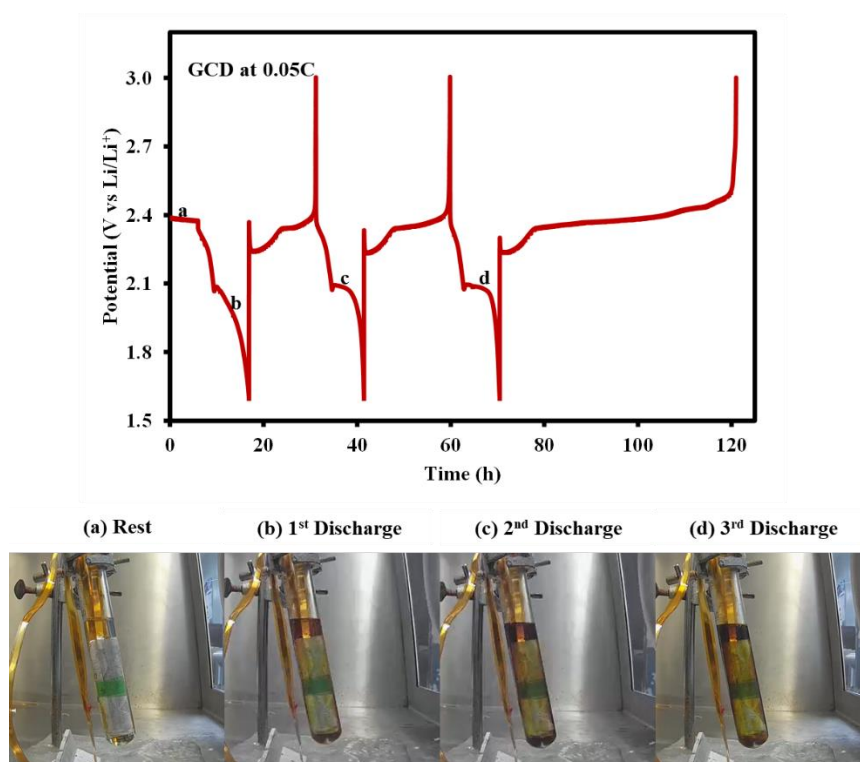


Fig. S5 the accumulation of higher concentration of the polysulfide dissolved into the electrolyte as time and number of cycles increase.

During the GCD (Galvanostatic charge-discharge) experiments, the electrolyte was closely observed. Over time, a noticeable color change was observed, transitioning from colorless to yellow. To document this observation, a video of the electrolyte investigation was set up. You can view the video from the links provided below:

Link to VDO

<https://www.dropbox.com/scl/fi/xvshit8oyr47323u5a49j/1-Cycles-LiS-Profile.mp4?rlkey=9qniupw9cu2ukoui20jh1puhs&dl=0>

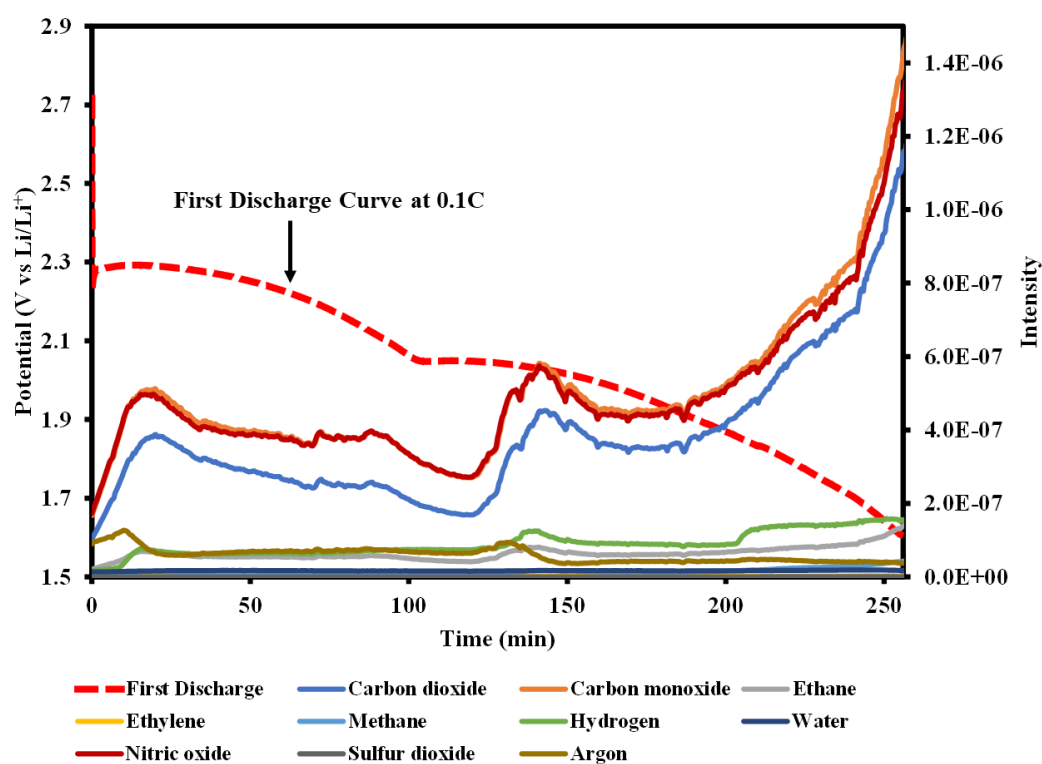


Fig. S6 The first discharge profile and relevant of the gases produced from the jelly roll.

The jelly roll was fabricated and subjected to GCD at 0.1C. During the first discharge, the gases produced were detected using differential electrochemical mass spectrometry (DEMS).

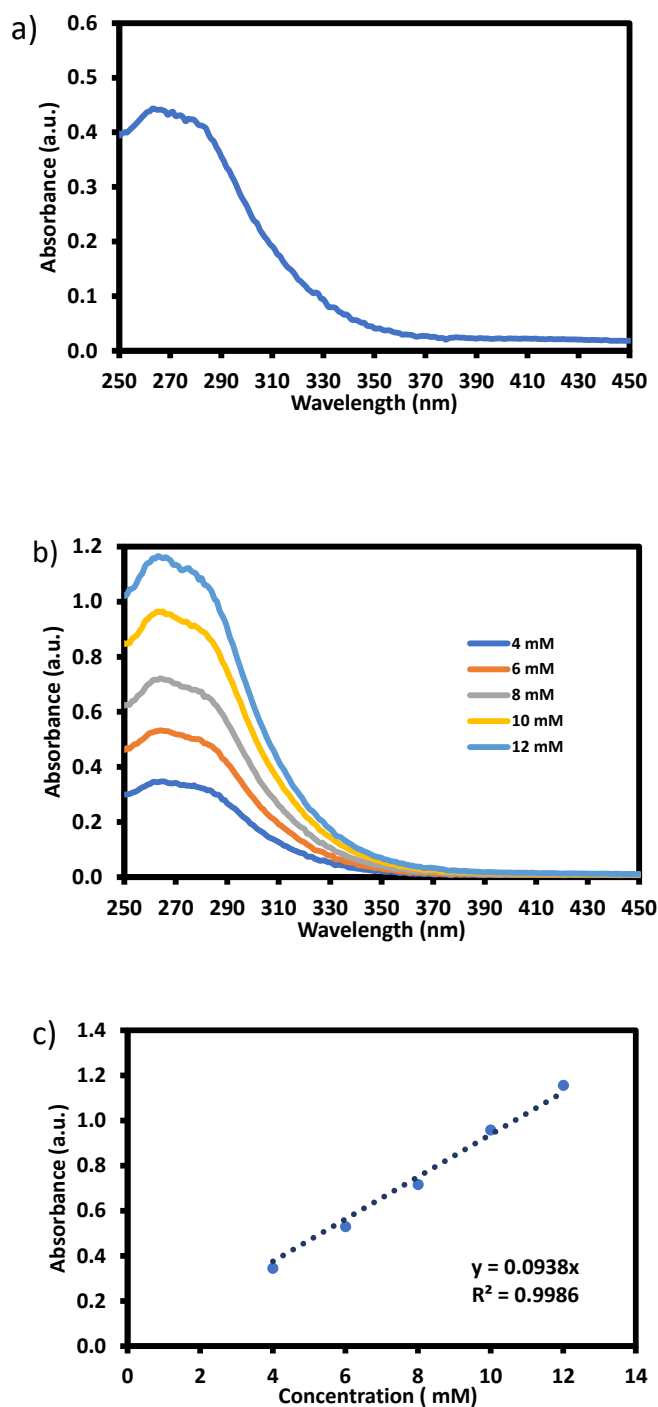


Fig. S7 UV-VIS absorption spectra of a) the electrolyte after cell cycling, b) the standard Li_2S_6 in varying concentration, and c) the linear calibration curve from the absorption of Li_2S_6 at 262 nm.

The electrolyte after cycling was collected and diluted in DOL:DME solvent to measure its absorbance. Fig. S7a illustrates the absorbance of the electrolyte sample, with the absorption peak at 262 nm corresponding to Li_2S_6 absorption via S_6^{2-} .¹ To determine the concentration of polysulfide, Li_2S_6 standard solutions were prepared at various concentrations by reacting sulfur powder with Li_2S in DOL:DME (1:1v/v) solvent, following the stoichiometric ratio: $\text{Li}_2\text{S} + 5/8\text{S}_8 \rightarrow \text{Li}_2\text{S}_6$, representing a mid-length chain polysulfide species. Polysulfide samples were prepared in the glove box at a concentration of 1M, and then they were diluted to lower concentrations. UV-Vis measurements were conducted using a seal cuvette. Fig. 7b illustrates the absorbance of the Li_2S_6 standard solutions, and Fig. 7c shows the linear calibration curve. Based on these measurements, our electrolyte sample collected after cell cycling was found to have a concentration of 1.17 M. This indicates that a high concentration of polysulfide dissolved into the electrolyte, leading to the loss of active material, the fading of capacitance, and ultimately resulting in battery failure.

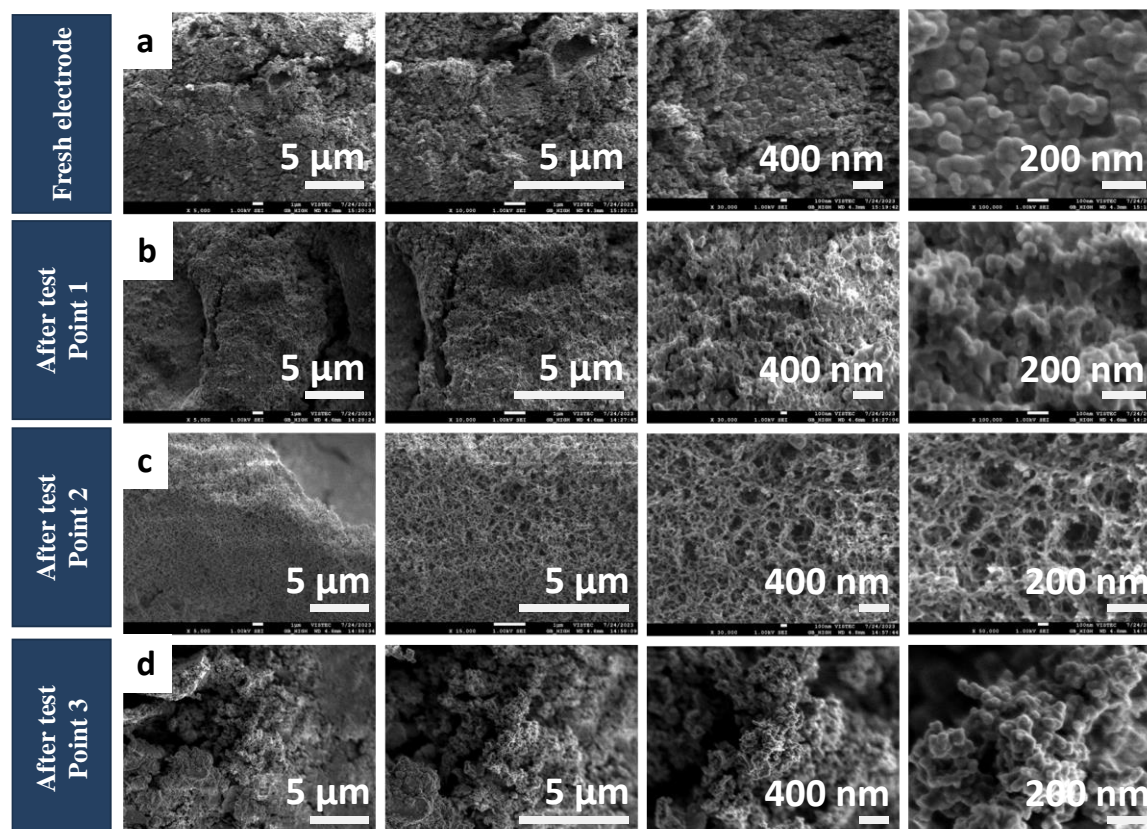


Fig. S8 FESEM images of the cathode a) before and b), c), d), after cell cycling at the position of the beginning, the middle, and the end of the roll.

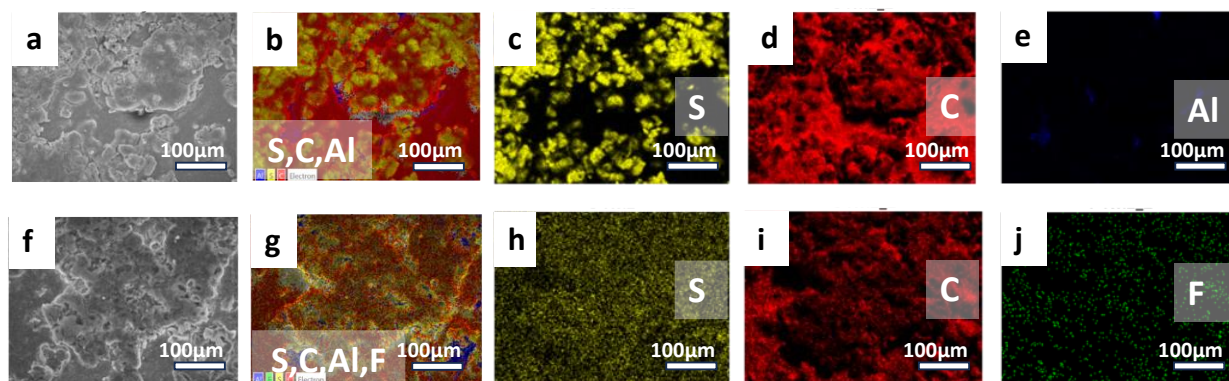


Fig. S9 SEM images of z) fresh cathode illustrating the element contains in b), c), d), e) and f) cathode after cycling f with EDX analysis illustrating elemental contains information in g), h), i), and j).

Reference

1. P. Chiochan, S. Kosasang, N. Ma, S. Duangdangchote, P. Suktha and M. Sawangphruk, *Carbon*, 2020, **158**, 244-255.