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## Method Article – Title Page

<b>Title</b>	Designing Reliable Electrochemical Cells for Operando Lithium-Ion Battery Study
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<b>Corresponding Author's email address</b>	<i>bjayan@andrew.cmu.edu</i>
<b>Keywords</b>	<ul style="list-style-type: none"><li>• <i>Window coin cells</i></li><li>• <i>Operando experiment</i></li><li>• <i>LiCoO<sub>2</sub> cathode</i></li><li>• <i>Si anode</i></li></ul>
<b>Direct Submission or Co-Submission</b>  <i>Co-submissions are papers that have been submitted alongside an original research paper accepted for publication by another Elsevier journal</i>	<i>Co-Submission</i>  <ul style="list-style-type: none"><li>• APEN-D-21-00562 (Title: Multiscale Operando X-ray Investigations Provide Insights into Electro-Chemo-Mechanical Behavior of Lithium Intercalation Cathodes)</li></ul>

### ABSTRACT

Operando experiments attract increasing attention in lithium-ion batteries (LIBs) studies for their ability to capture non-equilibrium and fast-transient processes during electrochemical reactions. They provide valuable information and mechanisms that cannot be obtained from ex-situ methods. Designing a suitable and reliable electrochemical cell is the first crucial step for most operando studies. A poorly designed in-situ cell introduces artifacts into the data and might lead to misleading results. Even though many in-situ cells have been designed and applied for operando studies, designing a reliable cell is not trivial, especially for long-term cycling experiments. This study introduces the steps and details of a specific type of in-situ cell, i.e., modified coin cell, that can be applied reliably in various operando experiments. The reliability of the modified coin cell is demonstrated by comparing its electrochemical performance with the standard coin cell. The modified coin cell is then applied in various operando experiments, including operando transmission X-ray microscopy and operando synchrotron X-ray scattering.

- Sealing the cell casing window with metal films maintains the overall electrochemical performance of electrodes.
- Depending on the operando experiment, the type of the coin cell and the window shape must be selected carefully.

### SPECIFICATIONS TABLE

<b>Subject Area</b>	Energy
<b>More specific subject area</b>	<i>Electrochemistry</i> <i>Lithium-Ion Battery</i>

<b>Method name</b>	<i>Customized coin cells for operando studies</i>
<b>Name and reference of original method</b>	<i>Bak, Seong-Min, et al. "In situ/operando synchrotron-based X-ray techniques for lithium-ion battery research." NPG Asia Materials 10.7 (2018): 563-580.</i>
<b>Resource availability</b>	<i>N.A.</i>

**\*Method details**

**Materials and Fabrication Procedure**

The fabrication procedure for a reliable window coin cell is illustrated in Figure 1. Figure 1a displays the components within a window coin cell. Figure 1b,c shows the detailed fabrication steps, as follows.

Step 1: Smearing a small amount of epoxy on window casings. A few tricks of this step are listed below.

- Window casing: It is recommended to use an automatic laser cutter to cut the coin cell casings. Ensure the edge of the window area is smooth and remove sharp leftover metals on the edge of the window if there are any. Also, selecting an appropriate type of coin cell is essential. The shape and the size of the window can be customized, depending on the operando experiment. For example, Figure 1d shows three pairs of window coin cell casings. Selecting/Designing a suitable window coin cell casing is the first step to ensure a successful operando experiment.
- Epoxy adhesive: Eccobond 45 and Catalyst 15 were selected in this study with an around 1:1 ratio. The Eccobond 45 and Catalyst 15 were added into a small container, followed by a hand stirring for 2-3 mins until the color transfers from clear (Ecocobond)/yellow (Catalyst) to milky.
- Amount of the epoxy adhesive: The amount of the epoxy adhesive added to the casing affects the cell performance. It is recommended to add as little as possible but cover the whole edge without an interspace.

Step 2: Seal the window with metal films. A few tricks of the step are listed below.

- Material selection for the sealing: Selecting the suitable material to seal the window is one of the most important steps to ensure a reliable window coin cell for the operando studies. Kapton film is generally applied to seal the window for in-situ coin cells [1]. However, our study shows that Kapton film sealing is not appropriate for long-term cycling experiments. Here, an Al film was used on the top casing (contact to the cathode), and a Cu film was selected to seal the bottom casing (contact to the anode).
- The thickness of metal film: The Al and Cu films used in this study has three functions: (1) seal the window, (2) provide electronic conductivity for electrodes, and (3) offer mechanical pressure for electrodes that will be used in an operating cell. A thick metal film provides better mechanical stress but reduces the X-rays attenuation length to the active materials that we are interested in. Thus, selecting the appropriate thickness of the metal film is essential, which needs to be determined based on the specific experiment and the X-ray sources. This study applied an 8  $\mu\text{m}$  thick Cu film and a 14  $\mu\text{m}$  thick Al film. The selection has been proven to be suitable for many different operando experiments.

Step 3: Press metal film on the casing. To apply uniform stress in all directions, we loaded a 20 g weight on the metal films for 3 minutes. This step helped the dispersion of the epoxy adhesive before it was solidified.

Step 4: Cure the epoxy at 50 °C for 6 hours. The Eccobond 45/Catalyst 15 mixture can be slowly cured at room temperature or rapidly cured at an elevated temperature. For reference, the cure time is 16 h – 24 h at 25 °C, is 4 h – 6 h at 45 °C, and is 2 h – 4 h at 65 °C [2].

- A trick at this step is to hang one side of the casing while curing. The epoxy can immerse through the window, which could stick the casing on the plastic container shown in Figure 1b.

Step 5: Assemble the window coin cell in an Argon-filled glovebox. Figure 1a shows the components in a coin cell, including two Li chips, an electrolyte-immersed separator, and a cathode electrode. We removed conventionally applied stainless steel spacer because it blocked the transport of lab X-rays. Due to the good malleability of Li metal, two Li chips could ensure good mechanical contact between the cathode and the anode within a coin cell after crimping. Additionally, the deformation of Li metals ensured good contact among different components within a coin cell. Figure 1c displays an assembled window coin cell.

Step 6: Store the window coin cell overnight in a fume hood. The crimping process of making a coin cell could break the window, leading to the leakage of electrolytes. As conventionally used electrolyte contains  $\text{LiPF}_6$ . It reacts with moisture in the air and generates HF, which is highly toxic to the human body. Additionally, storing the window coin cell helps the immersion of the electrolyte into electrodes. Thus, this step is crucial and is not recommended to be skipped when making window coin cells.

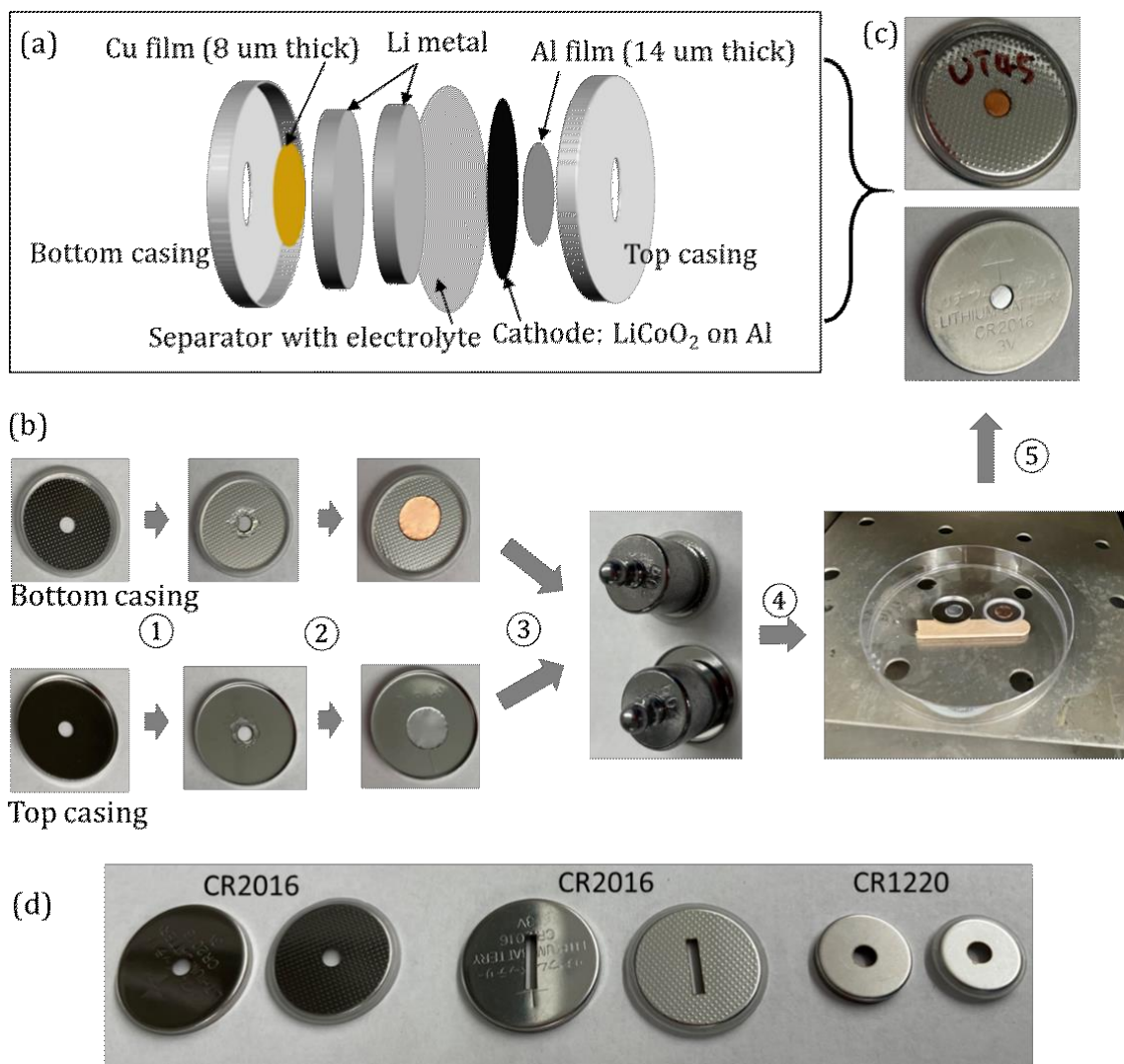


Figure 1. The steps of designing a reliable window coin cell for operando studies. (a) The components within a window coin cell. (b) The steps to seal the bottom casing and the top casing. (c) The images of an assembled window coin cell. (d) Different types of coin cell casings and windows. Selecting/Designing the appropriate casing and window is crucial for the success of operando experiments.

## Method Validation

The electrochemical performance of the window coin cells based on the abovementioned assembling steps is similar to the normal coin cells. Figure 2 compares the electrochemical performance, including rate capability and cycling stability, of a window coin cell and a normal coin cell. Figure 2a indicates that the window cell shows similar capacities as the normal cell at all the tested C-rates (C/3, 1C, 2C, 5C, and 10C). The capacity difference between the two types of cells is within the error bar among the three tested samples. Figure 2b further compares the discharge curves of the two types of cells at C/3, 2C, and 10C. Although their discharge capacities are close at the three tested rates, the discharge voltages of the window coin cell are lower, especially at high C-rates (2C and 10C). As the existence of the window or not is the only difference between the two types of cells, the larger overpotential in the window cell should be from the window and the sealing process. Even though electronically conductive Al and Cu films were applied to seal the window, the epoxy adhesive area was insulating, reducing overall conductivity. Additionally, the Al and Cu films were thin that cannot provide sufficient mechanical pressure between the cathode and the anode electrode compared to the stainless steel casing. Thus, it is reasonable that the window coin cell shows a larger overpotential during discharging than the normal coin cell in (Figure 2b). Optimizing the design can alleviate but cannot eliminate the effect, and such an effect needs to be considered when analyzing operando experimental data.

Figure 2c compares the cycling stability of the two types of coin cells tested between 3.0 V – 4.5 V at room temperature (20 °C) at a C-rate of C/2 [3]. The capacity degradation of the two types of cells almost overlapped with each other, suggesting that the casing window had a negligible effect on the cycling stability. Figure 2d shows the images of two window coin cells after being stored for one year. The surface of the cells is clean with no leaked electrolytes or side products. Thus, the Al and Cu film-sealed window coin cell is reliable for long-term storage and cycling experiment.

The window coin cells can be applied to various operando experiments. Figure 2e,f displays results from an operando transmission X-ray microscopy and an operando synchrotron-based X-ray scattering. More details of the experiments can be found in our recent paper [Error! Reference source not found.].

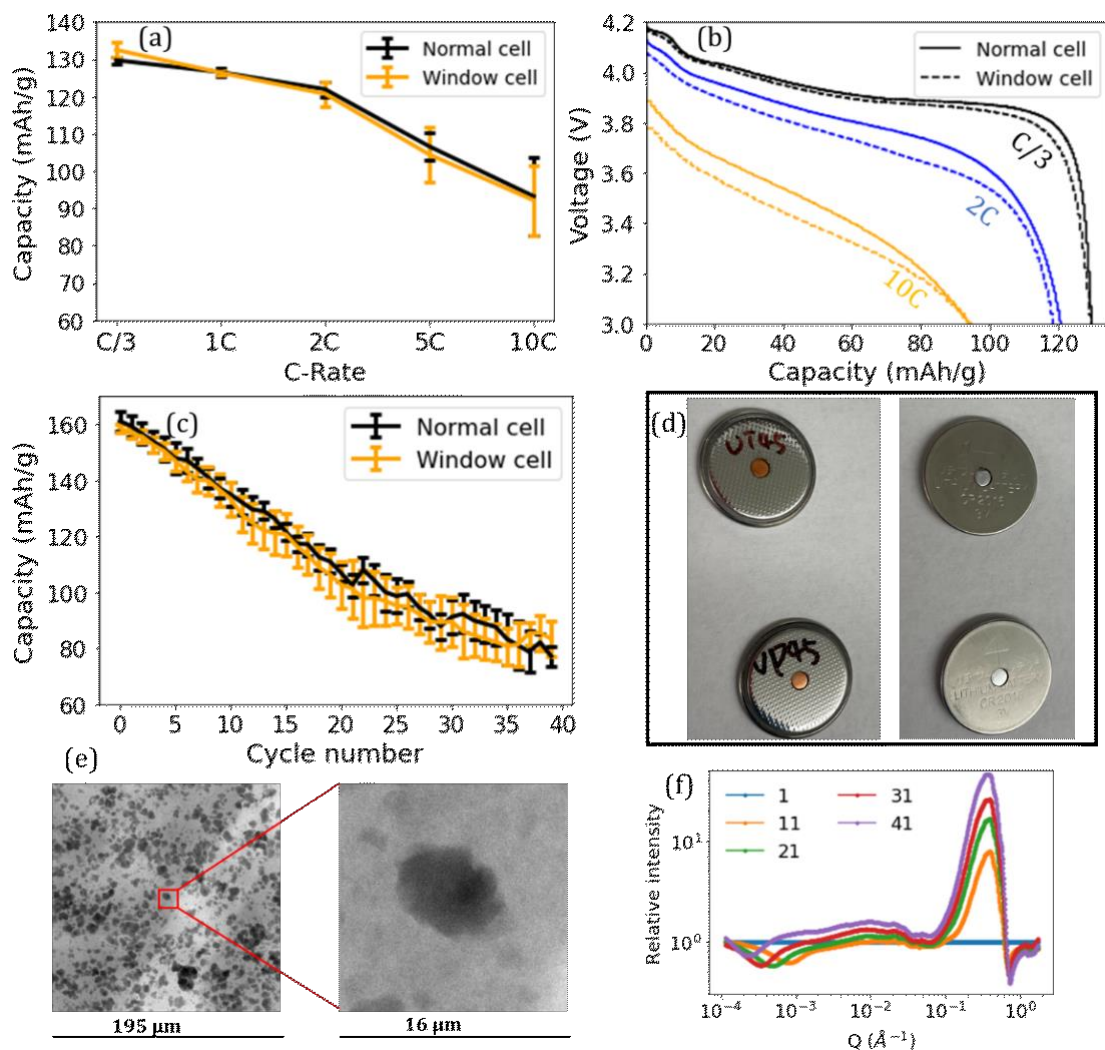


Figure 2. Performance comparison for normal coin cells and window coin cells. (a) Rate capability tested between 3.0 V – 4.2 V at room temperature (20 °C). Three cells are tested for both types of cells. (b) The discharge curves at C/3, 2C, and 10C for the two types of cells. (c) Capacity degradation during high-voltage cycling between 3.0 V – 4.5 V at C/2 and room temperature. (d) The appearance of two window coin cells after one year of storage. (e) Two microscopic images from an operando transmission X-ray microscopy experiment. (f) The result from an operando synchrotron X-ray scattering experiment.

## Comparing with Conventional Kapton Film Sealing Methods

Kapton film-sealed window coin cells have also been tested and compared with the metal film-sealed window cells, as shown in Figure 3 [1]. The Kapton film-sealed window cells are not reliable. After multiple trial-and-errors by using different epoxies and different thicknesses of Kapton films, their performance was still not comparable to the metal

films-sealed window cells (Figure 3b). For example, Figure 3a shows the first three cycles at C/10 of a metal films-sealed window coin cell. The voltage and the capacity are stable during cycling. In comparison, Figure 3c suggests that the capacity of a Kapton film-sealed window coin cell degrades quickly in the first three cycles. Additionally, a large voltage spike is observed at the cycle 2 and 3 at the beginning of the charging process for cells with the Kapton windows (Figure 3c). The appearance of such a spike could be from side reactions of electrolytes due to the leakage of the window. Thus, the metal sealing is much better than the Kapton seal in terms of electrochemistry performance.

Figure 3d further shows two Kapton film-sealed window coin cells after being stored for one year. Both cells cracked due to side reactions that happened within cells. It is believed that the moisture in the air can diffuse through the Kapton film, which can react with the electrolyte in the coin cell and trigger other side reactions. For an experiment that requires a Kapton film window, we recommend using a thick Kapton film ( $> 50 \mu\text{m}$ ) to slow down the moisture diffusion through the Kapton film, and thus reduce the failure speed of the window coin cell.

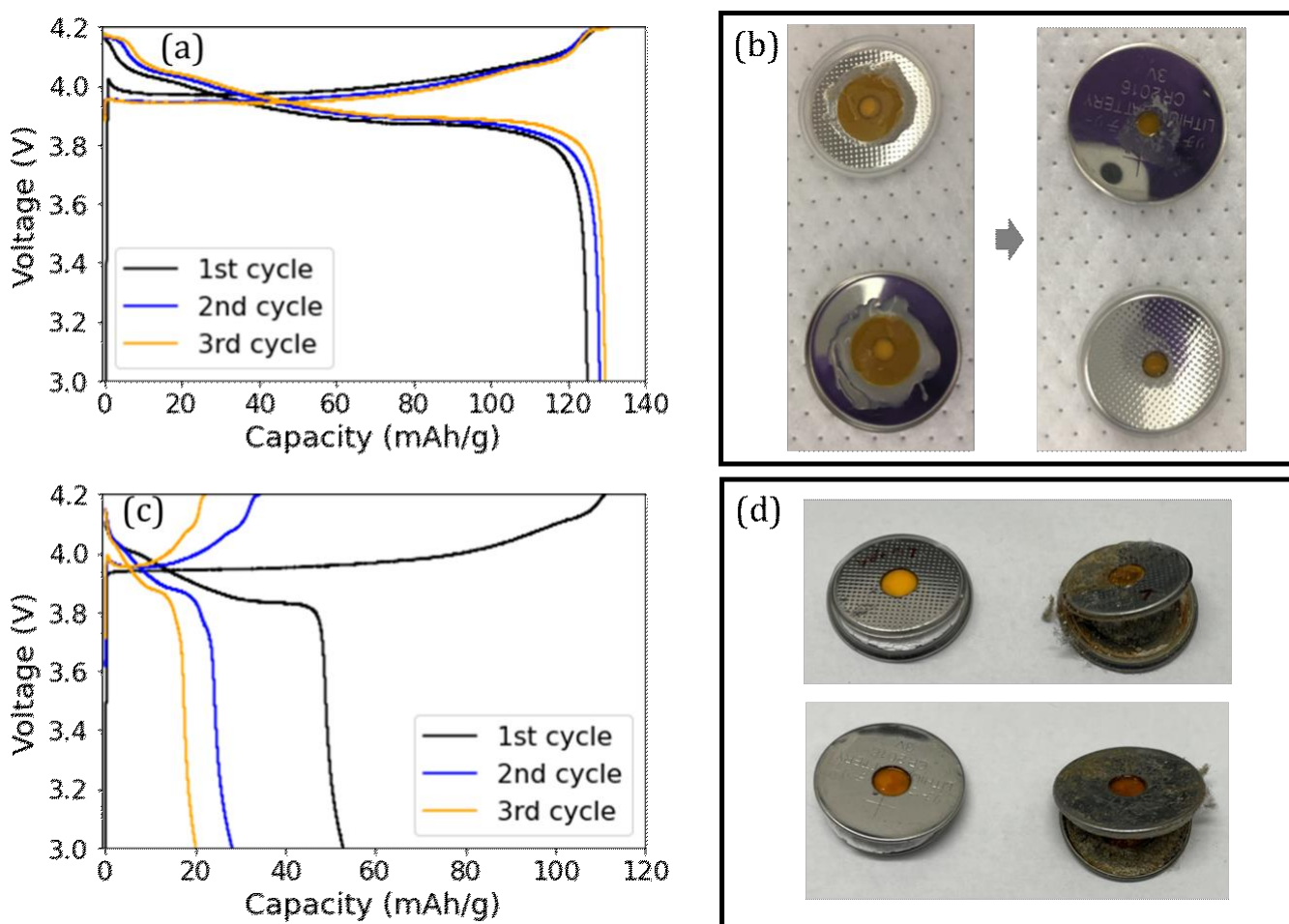


Figure 3. Comparing the performance of window coin cells using metal film and Kapton film for sealing. (a, c) The charge and discharge curves of the first three cycles in a window coin cell sealed by (a) metal films and (c) Kapton films at C/10. (b) The images of casings sealed by Kapton films and the corresponding assembled window coin cells. (d) The appearance of two window coin cells with Kapton film sealing after one year of storage.

### Kapton Film Windows for Tomographic Imaging Applications

One notable example of experiments that may benefit from a Kapton film window is tomographic X-ray imaging [4,6]. During a tomographic X-ray scan, a sequence of radiograph images is acquired as the sample is rotated with respect to the fixed X-ray beam. In the window coin cell configuration, this causes the effective thickness of the materials in the field of view to vary with the incident angle of the X-ray beam (i.e., thinnest at  $0^\circ$  and thickest at  $90^\circ$ ). Such variation

may be insignificant for imaging instruments that utilize high-energy X-rays, such as those at synchrotron facilities, as the X-ray attenuation lengths will be much longer. However, imaging with lab-scale X-ray instruments requires careful consideration of materials and their thickness as attenuation lengths are of similar order as those commonly used in coin cell fabrication (e.g., copper will absorb approximately 64% of 8 keV X-rays at 22  $\mu\text{m}$  thickness, whereas Kapton will need to be over 1100  $\mu\text{m}$  thick to absorb the same amount).

As previously stated, using a thick Kapton film is essential to mitigate the rate of degradation. Also, locally purging the Kapton window area with nitrogen gas is further shown to extend cell life. Figure 4a shows the modified CR1220 coin cell sealed with Kapton films (140  $\mu\text{m}$  thick) mounted on a 3D-printed sample mount with integrated gas lines. The two posts that hold the coin cell in place also serve as gas channels through which nitrogen gas can flow. CR1220 coin cells were chosen over CR2016 coin cells to minimize the footprint of the sample during rotation when configured as shown in Figure 4a; this consideration is crucial to ensure the maximum range of rotation angles, especially when using imaging instruments with restrictive sample loading area. In addition, a rectangular window, 8 mm in width and 1.5 mm in height, is selected to further improve the tomographic image acquisition angles. Figure 4c, d shows the first, second, and eleventh cycle of silicon composite (50 wt% silicon microparticle, 25 wt% conductive carbon, and 25 wt% polyacrylic acid binder) half cells without nitrogen purging and with nitrogen purging, respectively. The cell cycled with local nitrogen purging shows greater capacity as well as greater rate capability. Although the problems associated with the use of Kapton film are not eliminated, the improved cycle life and performance enable greater flexibility for in-situ and operando X-ray imaging with low-energy X-ray sources. Figure 4b shows the volumetric reconstruction of the silicon composite anode in its uncycled state. The low X-ray attenuation length of Kapton and the rectangular window shape allows for high signal-to-noise ratio X-ray imaging, which is essential for high-quality volumetric reconstructions.

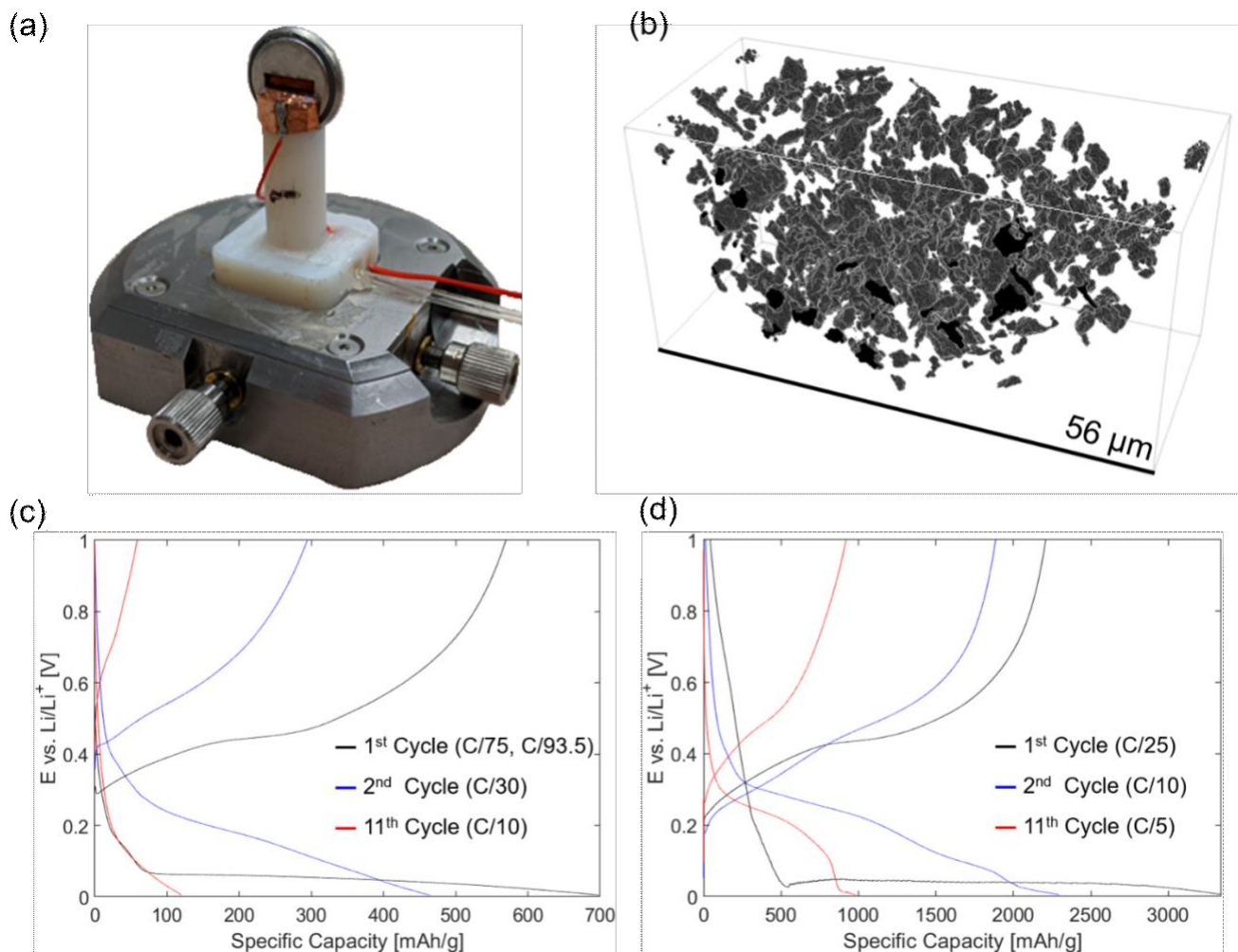


Figure 4 Performance comparison of Kapton film-sealed window coin cells with or without local nitrogen gas purging. (a) CR1220 coin cell modified with a rectangular window sealed with 140  $\mu\text{m}$  Kapton film mounted on a custom 3D-printed mount with integrated gas flow channels. (b) Volumetric reconstruction of a silicon composite anode obtained via in-situ X-ray tomographic scan using the setup shown in (a). (c, d) The charge and discharge curves of the first, second, and eleventh cycles in a Kapton film-sealed window coin cell with (c) without nitrogen purging and (d) with nitrogen purging. In (c), the discharge rate (C/75) and charge rate (C/93.5) do not match, as the charge rate was adjusted to counter the rapid degradation and low capacity of the initial discharge.

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**Declaration of interests:**

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.

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