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Note: Electrochemical cell for *in operando* X-ray diffraction measurements on a conventional X-ray diffractometer

Steffen Hartung,[1,2,3,a)] Nicolas Bucher,[1,2,3,a)] Ramona Bucher,[1] and Madhavi Srinivasan[1,3]
[1]*TUM CREATE, Singapore 138602, Singapore*
[2]*Technical University of Munich, Garching 85748, Germany*
[3]*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*

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Electrochemical *in operando* X-ray diffraction (XRD) is a powerful method to analyze structural changes of energy storage materials while inserting/de-inserting charge carriers, such as Li- or Na-ions, into/from a host structure. The design of an XRD *in operando* cell is presented, which enables the use of thin (6 μm) aluminum foil as X-ray window as a non-toxic alternative to conventional beryllium windows. Owing to the reduced thickness, diffraction patterns and their changes during cycling can be observed with excellent quality, which was demonstrated for two cathode materials for sodium-ion batteries in a half-cell set-up, P2-$Na_{0.7}MnO_2$ and $Na_{2.55}V_6O_{16}\cdot 0.6H_2O$. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4926465]

As electrochemical energy storage devices are being intensely researched for a variety of applications, approaches to optimize their performance are of high commercial interest. The underlying mechanism of energy storage for many systems is the intercalation of ions, e.g., Li^+ and Na^+, into a given crystal structure.[1–3] Thus, elucidating potential structural changes during (de-)insertion might go a long way in explaining observed electrochemical phenomena like capacity fading, and therefore deliver important information for better energy storage devices. Consequently, experimental setups have been developed to study these changes *in operando*.[4–6] For the observation of crystal structure changes, the method of choice is X-ray diffraction.

For electrochemical *in operando* XRD measurements, a setup needs to fulfill several requirements. An airtight system is crucial to prevent a reaction of air with the components of the electrochemical cell, particularly for half-cell setups that contain metallic lithium or sodium. The window, shielding the electrochemically active components from the outer atmosphere, should be as thin as possible and needs to have a low X-ray absorption coefficient to minimize X-ray absorption, and thus a decrease in signal intensity. Ideally, of course, non-toxic materials are preferred.

Even though commercial cell setups are available, they have some shortcomings. In a typical setup, the active material, which is to be measured during cycling in a half-cell setup with lithium or sodium as the negative electrode, is pressed onto the X-ray window. This is typically aluminum-coated beryllium, which serves both as current collector and as X-ray window due to its low X-ray absorption coefficient. Moreover, as the active material is mechanically pressed against the X-ray window, mechanical stability is desired to prevent fissures in the window. This can be achieved by using a rigid beryllium window with a typical thickness of around 125 μm. The main drawbacks of beryllium, however, are its toxicity and high cost. Furthermore, dissipating the current via the beryllium as it is the case in this setup makes the window more susceptible to electrochemically induced corrosion, as beryllium dissolves at voltages above 3 V.[7] After early studies by Chianelli *et al.* in 1978,[8] several approaches to tailor *in operando* XRD cells to specific needs have been proposed.[5,7,9–12]

This work presents a new cell setup developed by our group to address the obstacles for *in operando* diffraction measurements mentioned above. In this cell, the X-ray window and current collector are separated by a gap (see Figure 1 (8)). This setup has two main advantages. First, as the current is no longer dissipated via the X-ray window, corrosion is decreased and lifetime of the window, and thus possible *in operando* measurement time, can be extended. Second, mechanical pressure during cell assembly and subsequent cycling is no longer exerted on the X-ray window, but on the current collector. Thus, requirements in terms of mechanical stability can be greatly reduced for the X-ray window. As a consequence, beryllium can be replaced by the cheaper, non-toxic aluminum. Moreover, the thickness of the X-ray window can be reduced, so that X-ray reflection of the window material is minimized, and signal quality of the battery material is enhanced.

For the approach presented here, an aluminum foil with a thickness of 6 μm was used. The active material, together with teflonized acetylene black as binder, and activated carbon as conducting agent, was pressed into a stainless steel grid, which acted as the current collector (component (7) in Figure 1). After mounting the window (i.e., assembling parts (1)–(5)), the cell is turned around so that the inner part faces upward, and component (7) is placed onto (5), and then held in place by (13). A separator and lithium/sodium disc are placed onto (7), followed by a stainless steel spacer (12) in a floral shape—the outer edges touch the walls (component (13)), which inhibits lateral movement and prevents the electrodes from slipping out of position. The indentations ensure that the electrolyte, which is added after (12) is in place, can penetrate past the spacer and

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[a)] S. Hartung and N. Bucher contributed equally to this work.

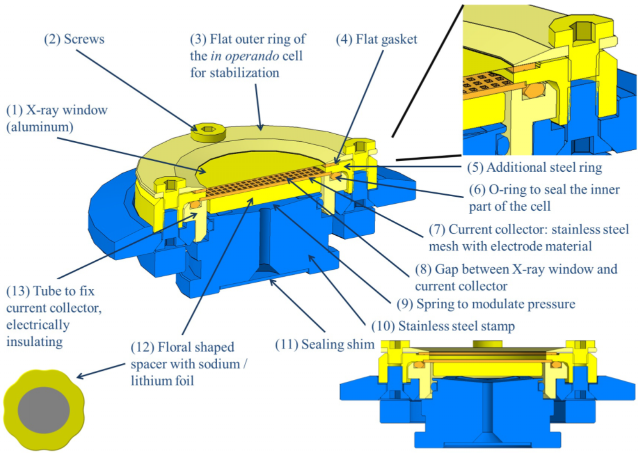

FIG. 1. Setup of the new *in operando* cell.

soak the separator and active material. These components are pressed together when closing the cell. Excess electrolyte can “leave” the inner part of the cell due to the indentations, which avoids pressure on the aluminum foil. Moreover, due to the steel ring (5), onto which the current collector is pressed, this pressure is accommodated without effect for the aluminum foil. For the lower part (blue (color code refers to online version) components in Figure 1), a setup rebuilt from a conventional commercial setup was used.[13] X-ray diffraction is measured in reflection mode from above, as the active material to be measured is exposed to X-rays due to the use of a stainless steel mesh. As the active material is slightly below the X-ray window, the outer stainless steel ring (3) needs to be flat to avoid reflection of incoming X-rays by the ring at small angles.

This *in operando* cell setup has been tested for various materials on a conventional Rigaku SmartLab X-ray diffractometer (200 mA, 45 kV) in reflection mode, with copper as X-ray source. One example is P2-$Na_{0.7}MnO_2$ (NMO), a promising material for sodium-ion batteries.[14,15] Figure 2 shows the X-ray diffraction patterns of NMO in powder form, and of a pellet, which was prepared in the way described above and built into the *in operando* XRD cell; the pattern of the aluminum used as X-ray window is added as reference. As can be seen, the pattern is well visible. The high signal intensity and excellent signal-to-noise ratio allow the monitoring of shifts of the observed reflections, or phase transformations, during cycling. The X-ray window does not reduce signal intensity detrimentally, and the well-defined reflections of the aluminum only hinder analysis in the rare case when a material has reflections in the same narrow angle range.

A good example for the easily observable shifts of the observed reflections is $Na_{2.55}V_6O_{16}{\cdot}0.6H_2O$,[16] which was cycled vs. Na in the presented setup with 1M $NaClO_4$ (Sigma Aldrich, >98%) in ethylene carbonate: propylene carbonate (1:1 % wt) as the electrolyte (PC: Sigma Aldrich, 99.7%, EC: Sigma Aldrich, 99%).

Figure 3(a) shows the XRD pattern of a $Na_{2.55}V_6O_{16}{\cdot}0.6H_2O$ pellet in the *in operando* cell. Figure 3(b) shows reversible shifts during electrochemical cycling for selected reflections in the range of $2\theta = 26.5°–31°$, which comprises reflections of diverse intensities. The color code represents the height profile, with blue (color code refers to online version) being the “noise,” i.e., only background reflection.

As can be seen, reversible shifts of the observed reflections are clearly observable, which can give new insights into changes of the lattice parameters, and thus enhance the understanding of the expanding and shrinking unit cell

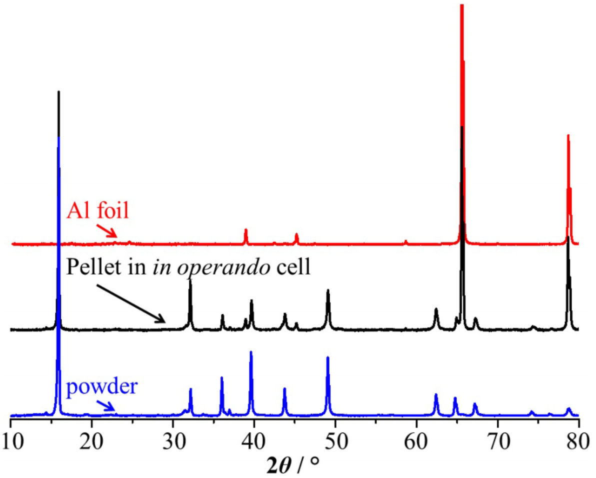

FIG. 2. X-ray diffraction pattern of P2-$Na_{0.7}MnO_2$ powder (bottom), a pellet with P2-$Na_{0.7}MnO_2$, teflonized acetylene black, and activated carbon (8:1:1 weight) on a stainless steel grid in the *in operando* cell (middle), the aluminum window (top).

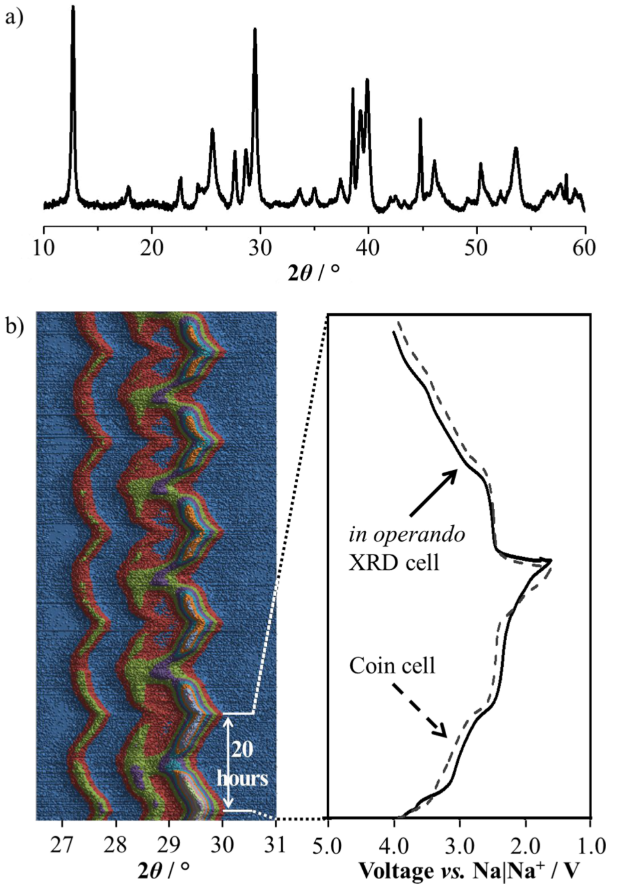

FIG. 3. (a) XRD pattern of $Na_{2.55}V_6O_{16}{\cdot}0.6H_2O$ in the *in operando* cell; (b) *in operando* XRD measurement for 5 cycles at 10 mA g^{-1}; left: reversible shifts of the observed reflections, right: representative charge/discharge curve in the *in operando* cell (solid line) and in a coin cell (dashed line).

during Na-ion insertion and de-insertion. This can be nicely correlated to the electrochemical charge/discharge data as presented on the right side of Figure 3(b), which also corresponds well with similar measurements in an established coin cell setup (solid line: *in operando* cell, dashed line: coin cell). Quantitative analyses to study this from a scientific, not instrument-focused point of view will be concluded shortly.

In summary, we have designed, constructed, and verified a new setup for electrochemical *in operando* X-ray diffraction measurements using a conventional X-ray diffractometer. The setup is based on a separation of X-ray window and current collector, which enables the use of non-toxic and cheap ultrathin aluminum foil, and thus ensures excellent signal quality. This facilitates the examination of structural changes while electrochemically inserting/deinserting Li- and Na-ions into/from a host material. Consequently, a deeper understanding for structural processes during charging/discharging battery materials can be obtained. These insights can be used to develop strategies to mitigate capacity fading in energy storage materials.

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