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Towards combined *operando* characterisation of advanced alkali metal batteries

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Summary

With the help from the funding, the two major steps of the project have been achieved:

1. A three-electrode cell setup that preserves the electrochemical properties of two-electrode full-size cells with the same experimental parameters
2. A cell design for *operando* diffraction and/or spectroscopic measurements that preserves the electrochemical properties of two-electrode full-size cells with minimum adjustment in experimental parameters

Although a combination of both cell setups has not been realised yet due to the lack of a suitable cell holder on the X-ray diffractometer, the combination should be straight-forward since both setups are based on commercial coin cells, with modifications in different parts of the coin cells. The results from the two above-mentioned steps will be elaborated in the following section.

We have before the 31st of October spent 198 000 SEK on this project.

Results

1. Development of the three-electrode cell setup

   As pointed out in the proposal, adding a reference electrode enables the measurement of individual resistance/impedance of the positive and negative electrodes. However, adjustments have to be made to accommodate the extra electrode in the cell. This is most commonly done in a pouch cell setup in the literature due to its flexibility, but the vacuum sealing process makes it difficult to control the electrolyte volume in the cell. Therefore, a customised cell format was considered in the proposal, the HS-3E cell from Hohsen Corp., Japan. After the project was granted, Hohsen Corp. released a new model, HS-3E-TK. Both models were purchased and tested. The feasibility of modifying the models for the operando spectroscopic/diffractometric measurements of the electrodes was also evaluated.

   The performance of the customised cells was, however, not close to the commercial coin cells, as shown in Figure 1. With the commercial coin cell as the benchmark, it can be observed that both the pouch cell and HS-3E cell showed much faster degradation in the specific discharge capacity. Despite several attempts, of which the one with longest cycle life is plotted in Fig. 1, we could not get stable cycling results from the HS-3E-TK cell. Given the fast increasing resistance of the customised cells from Hohsen Corp. as demonstrated in Figure 2, it can be assumed that the cells may not be sealed well enough so that the electrolyte is drying up at a much higher rate. The method of resistance measurement and the effect of electrolyte amount on the Li-S system can be found in the references[1,2]. This also seems to be an issue for the pouch cell but at later cycles. The main issue with the problem of the pouch cell remains to be the unknown amount of electrolyte loss during the vacuum sealing process, which may result in the scattering results in the initial cycles and faster capacity degradation.

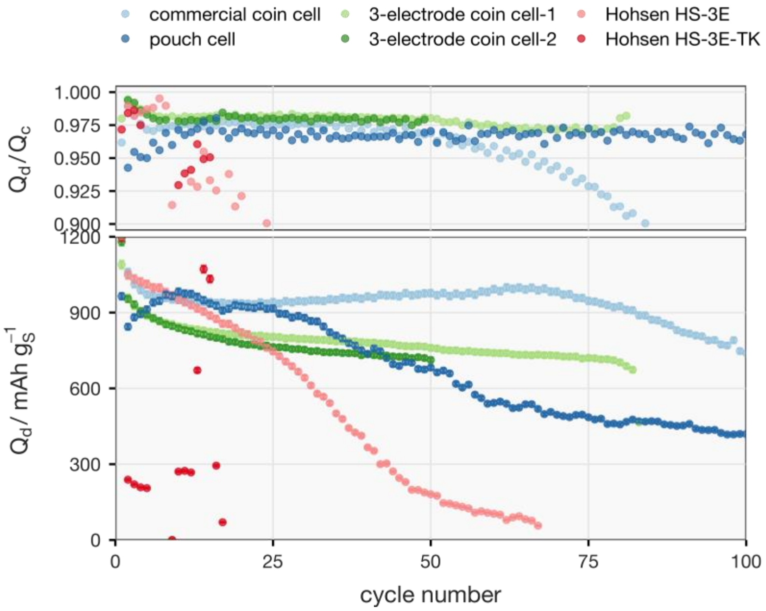

Figure 1 Specific discharge capacity (Q_d) and Coulombic efficiency (Q_d/Q_c) of the tested cells plotted against cycle number. The following data are left out of the plot for clarity. The Coulombic efficiency of HS-3E after the 25th cycle is below 0.9 and decreasing. The commercial coin cell and pouch cell cycled beyond the 100th cycle with both Coulombic efficiency and discharge capacity dropping. The 3-electrode coin cells are still cycling at the time of writing of this report.

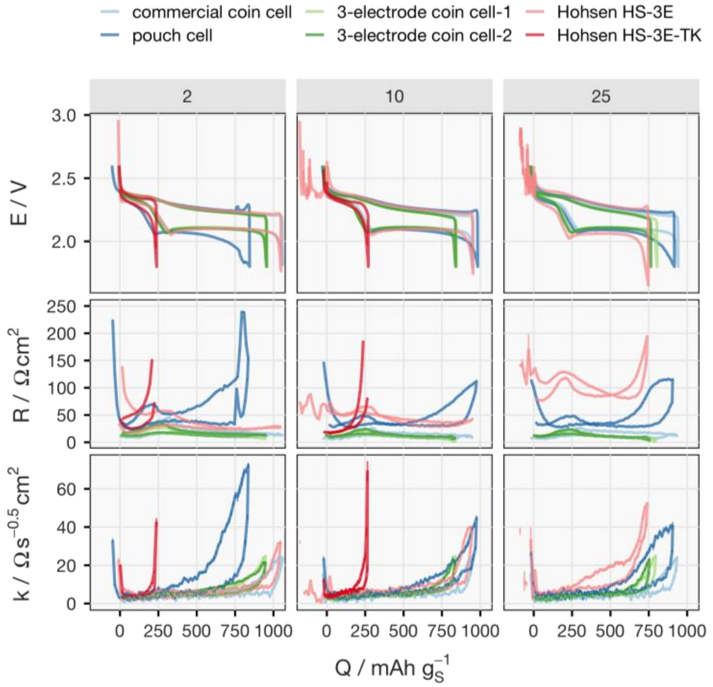

Figure 2 Cell voltage (E), internal resistance (R) and diffusion resistance coefficient (k) of the cells plotted against state of charge (SoC) represented by the specific capacity (Q) in cycles 2, 10 and 25. The following data are left out of the plot for clarity. R values of HS-3E-TK near 250 mAh g_S^{-1} are above 250 Ωcm² in cycles 2 and 10. The k values of HS-3E at the end of charging ($Q < 0$ mAh g_S^{-1}) are below 0 Ωs$^{-0.5}$cm².

Considering the issue with controlling the electrolyte amount for both the pouch cell and customised cells, we decided to try to insert the reference electrode into a commercial coin cell. Aiming for the minimal modification and disturbance of the cell setup, 50 μm thick polyimide-insulated gold wire was chosen to be the reference electrode,[3] which is inserted into the electrode stack inside the coin cell and goes between the upper casing and the plastic gasket of the coin cell to the outside.[4] The tip of the reference electrode inside the cell can be in-situ lithiated to form lithium gold alloy, which has a stable potential around 0.3 V vs. Li/Li$^+$,[5] which was done for 3-electrode coin cell-2. In 3-electrode coin cell-1, the feasibility of using the pristine gold wire as a quasi-reference electrode was investigated.

In Fig. 1, the two three-electrode coin cells demonstrated very similar cycling behaviours. They both showed lower specific discharge capacity compared to the commercial coin cell, but both Coulombic efficiency and discharge capacity are stable for at least 50 cycles. The lower discharge capacity may be a consequence of the extra electrolyte added to the cell to account for the extra separator required, which was also done for the customised and pouch cells. The extra electrolyte volume was calculated based on the volume and porosity of the separator, but this may be an overestimation since the polyolefin-based separator may not be fully wetted. The effect of extra electrolyte can also be accounted for the slightly lower internal resistance of the 3-electrode coin cells compared to the commercial coin cell in Fig. 2.

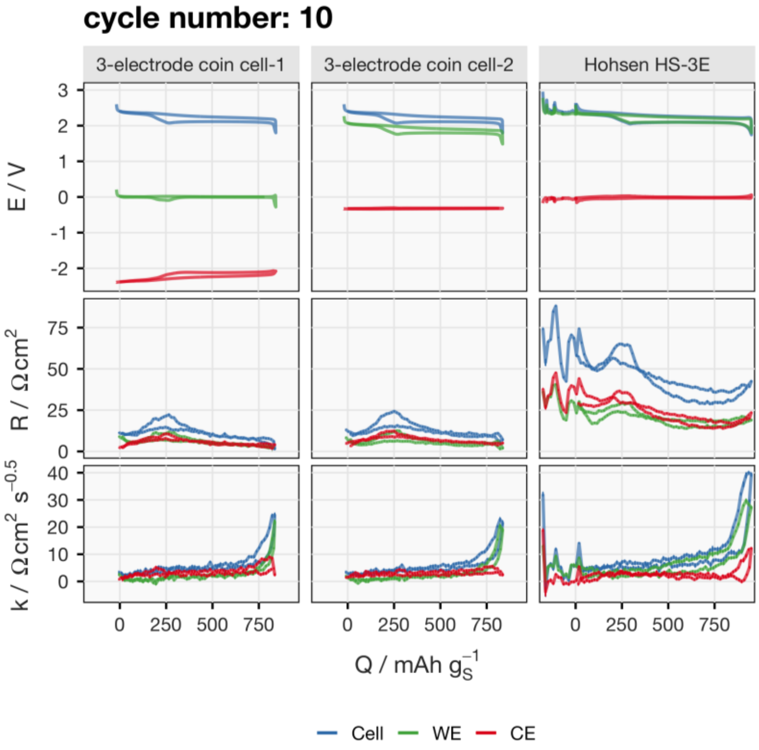

Figure 3 Cell voltage (blue), potentials of the working electrode (WE) and counter electrode (CE) measured against the reference electrodes in the tenth cycle, followed by the internal resistance (R) and diffusion resistance coefficient (k) derived from each voltage measurement, respectively. The reference electrodes are Au, LiAu alloy and Li in 3-electrode coin cell-1, 3-electrode coin cell-2 and Hohsen HS-3E, respectively.

The potentials of the working and counter electrodes can be measured separately in the three-electrode cell, as displayed in Figure 3, from which the individual resistance contributions from each electrode can be derived. Different reference electrodes were used in the cells because of the cell-setups, resulting in the different potential profiles of the working and counter electrodes in the three cells. Nonetheless, the resistances of each electrode in the cells follow the same trend, which even have almost the same values in the coin cells. The internal resistance (R) is mostly equally divided between the working and counter electrodes while the diffusion resistance coefficient (k) is mostly contributed by the working electrode in this cycle. The individual resistances of the HS-3E cell are substantially higher than that of the coin cells due to the much higher cell resistances as seen in Fig. 2, for the reasons discussed in the last paragraph.

Both pristine and lithiated gold, used in 3-electrode coin cell-1 and 3-electrode coin cell-2, rendered very close resistance values by the Intermittent Current Interruption (ICI) method.[1] This indicates that the pristine gold, serving as a quasi-reference electrode, can maintain a stable potential during the short measurement time (1 s) of the ICI method even though it does not hold a stable potential over the whole period of cycling. This short-term stability could be a result of the soluble reaction intermediates at the positive electrode (lithium polysulfides) acting as a depolariser in the electrolyte. However, for longer measurements, e.g. electrochemical impedance spectroscopy, a true reference, such as the LiAu alloy in 3-electrode coin cell-2, is required. As shown in Fig. 3, the potential between the counter (Li) and reference (LiAu) electrodes maintained almost constant at – 0.3 V throughout the cycle.

2. Development of the cell setup for *operando* X-ray diffraction measurements

Among the various spectroscopic/diffractometric techniques that can be coupled with electrochemical experiments, *operando* X-ray diffraction (XRD) was chosen to be our first aim since it is widely utilized across different cell chemistries for electrochemical energy storage systems. In the literature, the most common cell for *operando* XRD is also pouch cell due to the low X-ray absorption of the pouch material. However, as discussed previously, the electrolyte volume cannot be controlled in a pouch cell. Given the possible electrolyte leakage issue with the customised cells and the success with the three-electrode coin cells, the direction of development was set to the modification of coin cells for *operando* XRD measurements.

The first generation of our modified coin cell has been utilized in our published work,[2] where a detailed description of the modification can be found. In short, circular holes were drilled on the stainless steel coin cell casings, then sealed with polyimide films. The stainless steel spacer inside the cell was replaced with beryllium discs, which has much lower X-ray absorption but still maintain the stack pressure. However, with only polyimide film, the sealing of the windows was not ideal, especially in the long term. Therefore, we improved the window by using aluminium-coated polyimide films, resulting in higher cycling stability of the operando cells, as shown in Figure 4. The operando XRD measurement with the voltage and resistance profiles of an example are plotted in Figure 5. Compared to the previous work,[2] the new cell has much lower resistances, which are very similar to the resistances of the commercial coin cell in Fig. 2. The new window material with lower absorption also enables the XRD measurement of thinner electrodes, which generates lower diffraction intensity, and shorter collection time, resulting in better time resolution.

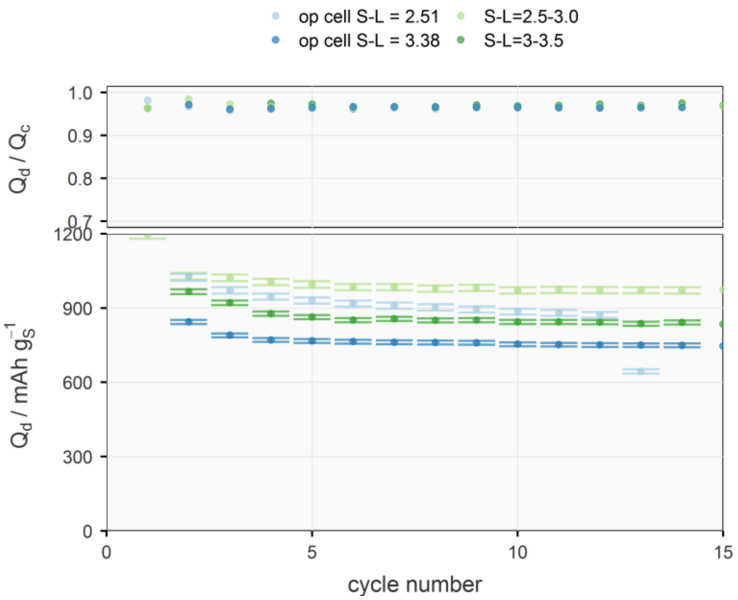

Figure 4 Specific discharge capacity (Qd) and Coulombic efficiency (Qd/Qc) of the tested cells plotted against cycle number. "S-L" denotes sulfur-loading in the unit of “mg$_S$ cm^{-2}” and "op cell" denotes the modified coin cells. The other two cells are commercial coin cells.

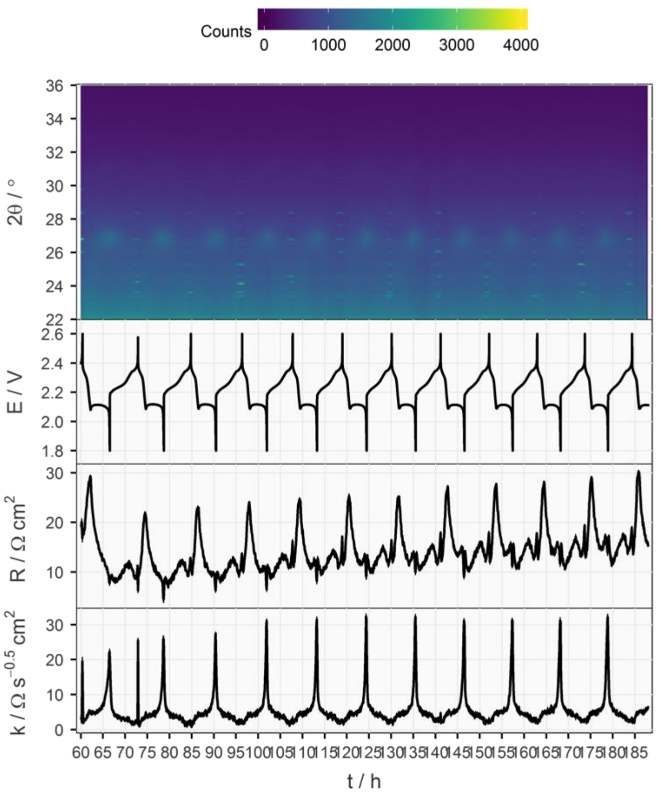

Figure 5 Operando XRD measurement of the "op cell S-L = 2.51" cell. The heatmap on the top shows a part of the diffraction pattern evolving with the cycling time. The electrochemical data, cell voltage (E), internal resistance (R) and diffusion resistance coefficient (k), are plotted against cycling time below.

Outlook

As elaborated above, this project has demonstrated two straight-forward modifications of commercial coin cells. One allows the insertion of the reference electrode. The other enables the measurement of X-ray diffraction with high signal-to-noise ratio and short collection time. The combination of both modifications should be simple since both modifications are easily executable and at different parts of the cell, thus not interfering with each other. The only unaddressed issue is the design of a suitable cell holder to mount the cell onto the XRD diffractometer and allow a stable connection for the reference electrode. Nevertheless, this issue should be easily resolved through the collaboration with the mechanical workshop.

References

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