Highly sensitive operando pressure measurements of Li-ion battery materials with a simply modified Swagelok cell

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**Abstract:**

A new cell design has been developed using a standard Swagelok cell for Li-ion battery material characterisation, which has been modified by replacing one of the electrode cylindrical plungers with an adaptor to a pressure sensor. By simplifying the cell design (no valves or unnecessary connectors have been included), the cell headspace volume is kept at a minimum (ca. 1.9 ml for a one-inch-diameter cell) which produces a dramatic increase in sensitivity of the measurements with respect to conventional set-ups. Changes in pressure induced by Li-ion battery materials processes (gas evolution, structural changes in volume of the battery material due to Li-ion insertion/extraction) are monitored with unprecedented sensitivity. Here we illustrate the application of this novel cell design for the operando pressure measurements of LiFePO4 and graphite in Li half-cell configurations, and detailed procedures of cell calibration, protocols for cell preparation and assembly and technical drawings of the cell parts are provided to facilitate the adoption of this technique for testing new battery materials. We also demonstrate the high sensitivity of this new set-up to study the corrosion of cell materials in contact with LiPF6-containing electrolytes, which had not been explored before with operando pressure measurements.

**Introduction**

The process of lithium ion insertion and extraction into a host material structure produces changes in the volume of the crystallographic structure, and the associated stress and strain propagates through the porous composite electrode producing changes in the electrode volume and the cell volume.1–6 Changes in the crystallographic structure have been studied with X-ray and neutron diffraction;7–10 changes in the electrode volume and morphology have been studied with dilatometry11–13 and tomography;14–17 and changes in the cell volume have been studied in pouch cell designs using displacement sensors18–21 and buoyancy apparatus based on the Archimedes’ principle.22–26

Commercial Li-ion cells have been designed to be able to sustain reversibly the volumetric changes induced by lithium ion insertion and extraction for thousands of cycles of charge and discharge. However, irreversible changes in volume (due to, for example, gas evolution or collapse of the electrode structure) produce dramatic losses in performance. Indeed, monitoring the reversibility of the volumetric changes associated with Li-ion cell cycling has been identified as one of the most important predictors of the cell cycle life.27,28 Unfortunately, most of the techniques developed to monitor changes in volume of Li-ion cells are only applicable to commercial or pouch cell designs, whose fabrication require special facilities. In contrast, the investigation of new materials for Li-ion battery applications is usually done in coin cells or Swagelok cells, which are available in most research laboratories, and their fabrication can be carried out with electrode sheets prepared with small amounts of materials, thus enabling the screening of a wide range of electrode materials.29,30

Tarascon and coworkers developed a highly reliable Swagelok cell design to study the consumption and formation of gases in metal-oxygen batteries.31 While the cell design enabled reliable and long-term operando pressure measurements of metal-oxygen batteries, the application of such set-up to Li-ion battery studies would be difficult. The set-up had a total cell headspace volume of ca 8.8 ml for the cell connected to a pressure sensor, and enabled the use of 12 mm-diameter electrodes (in a half-inch-diameter Swagelok cell), which gives a ratio of cell headspace volume to electrode area of ca. 7.8 ml cm-2. To illustrate the need of higher pressure sensitivity for studying Li-ion battery materials, it is useful to consider the process of formation of an SEI on graphite, which is one of the Li-ion battery reactions producing the highest amount of gas evolution. The formation of an SEI on graphite produces around 2 µl of gas per mg of graphite.32,33 For a graphite electrode with loading of 6 mg cm-2, relevant to commercial batteries,29,30 the formation of an SEI would induce a change in pressure of only 1.5 mbar if cell headspace volume to electrode area is 7.8 ml cm-2 (ΔP ≈ 1 bar \* 2 x 10-6 l mg-1 \* 6 mg cm-2 / 7.8 x 10‑3 l cm-2 = 0.0015 bar; see equation (1) below).

Previously, Luntz and coworkers reported a powerful and versatile custom-made cell design to study metal-oxygen batteries.34 In this case, the cell had a total headspace volume of ca. 1.7 ml (when connected to the pressure sensor) and enabled the use of 12 mm-diameter electrodes, giving a headspace volume to electrode area ratio of ca. 1.5 ml cm-2. This lower ratio of headspace volume to electrode area results in a higher sensitivity for the detection of small amount of gases formed or consumed, but still, a modest change of pressure of around 8 mbar would be expected for the process of formation of an SEI on a graphite electrode with loading of 6 mg cm-2 (ΔP ≈ 1 bar \* 2 x 10-6 l mg-1 \* 6 mg cm-2 / 1.5 x 10‑3 l cm-2 = 0.008 bar; see equation (1) below).

More recently, Janek and coworkers reported a custom made cell design to monitor pressure changes during cycling of Li-ion battery materials.9,35–37 The cell had a total headspace volume of 4.1 ml (when connected to the pressure sensor) and enabled the use of 40 mm-diameter electrodes, thus giving a ratio of headspace volume to electrode area of 0.47 ml cm-2, which enables very highly sensitive measurements of gas evolution/consumption. This powerful cell design has been applied to study NMC523/graphite,35 LNMO/graphite,36 LTO/Li and NMC622/graphite,37 prelitiated LTO/graphite,9 prelitiated LTO/silicon38 and prelitiated LTO/LiNiO239 battery material combinations. Berg and coworkers also reported a highly sensitive cell set-up to perform operando pressure measurements of battery materials, which they applied to study LTO/Li,40 LNMO/Li,41 and supercapacitors.42–44

Here we report an alternative cell design with a similar sensitivity, which has the advantage of employing commercial Swagelok cell parts, and thus, it is more affordable and easy to implement in any battery research lab. This new cell design has a total headspace volume of ca. 1.9 ml (when connected to the pressure sensor) and enables the use of 25 mm-diameter electrodes (in a one-inch-diameter Swagelok cell), thus giving a headspace volume to electrode area ratio of 0.39 ml cm-2. Compared to other operando pressure Swagelok cell designs reported in the literature,31 this new approach provides an unprecedented sensitivity due to this very low value of the headspace volume to electrode area. Indeed, we report a change of pressure of ca. 40 mbar associated to the process of formation of an SEI on a graphite electrode with loading of 6.5 mg cm-2. We also report operando pressure measurements of LiFePO4 electrodes in Li half-cell configuration, and we demonstrate that the enhanced sensitivity of the present set-up also allows quantifying the volumetric changes of the electrodes induced by the electrochemical cycling.

In order to facilitate the wide adoption of this new cell set-up, we provide technical drawings of the cell parts and details of a procedure for the evaluation of the headspace volume, which is required for the quantitative analysis of the data. We also demonstrate that, due to the high sensitivity of the set-up, reactions of the cell parts (made of stainless steel) in contact with the LiPF6-containing electrolyte produce small amounts of gases that are observed in the operando pressure measurements. This shows the potential of this technique to study the stability of cell materials for battery applications. In addition, we also provide recommendations of careful polishing and drying procedures for cell parts, which enable the acquisition of stable operando pressure measurements revealing quantitative information of the volume changes associated with electrochemically induced reactions of lithium insertion/extraction.

2. Experimental methods

2. 1. Cell design

Figure 1a shows a sketch of a standard Swagelok cell used for Li-ion battery materials characterisation, and figure 1b shows our modified cell designed for operando pressure measurements. One of the cylindrical plungers that acts as current collector has been replaced by a home-made current collector containing an small hole, which has been filled with 1/8 inch tubing to minimize the volume of the hole, and the tubing has been brazed to the stainless steel cylinder at the external surface (opposite the location of the electrodes) in order to prevent any contamination inside the cell with the soldering material. The 1/8 inch tubing connects directly to a pressure sensor (PA-33X, Keller Druck AG) using standard Swagelok connections (Stainless Steel Swagelok Tube Fitting, Female Connector 1/8 in. Tube OD x 1/4 in. Female ISO Parallel (Gauge) Thread). A technical drawing of the home-made current collector is supplied in the supplementary information (section 1).

The modified cell design is connected to the pressure sensor inside an argon-filled glovebox (MBraun, Labstar, <1 ppm O2, <1 ppm H2O), which overcomes the need of using valves to seal the cell prior to its connection to the pressure sensor. The absence of valves in the cell design contributes to decreasing the total headspace volume of the cell when connected to the pressure sensor, which improves the sensitivity of the measurements. The spring and hollow cap to hold the spring were also removed in order to decrease the cell headspace volume further, and as a result, the assembly of the cell had to be done more carefully by placing the current collectors perpendicular to the electrodes in order to apply a homogenous pressure.

The cell body is a one-inch-diameter Swagelok 316 stainless steel union. Nylon ferrules are used to seal the cell, since it was found that it was easier to reliably obtain a gas-tight seal than with PTFE ferrules (note that metal ferrules are unsuitable since they produce electrical contact of the electrodes with the cell body, and hence, the short-circuit of the cell). The homemade current collector for operando pressure measurements was made of 316 stainless steel (RS components).

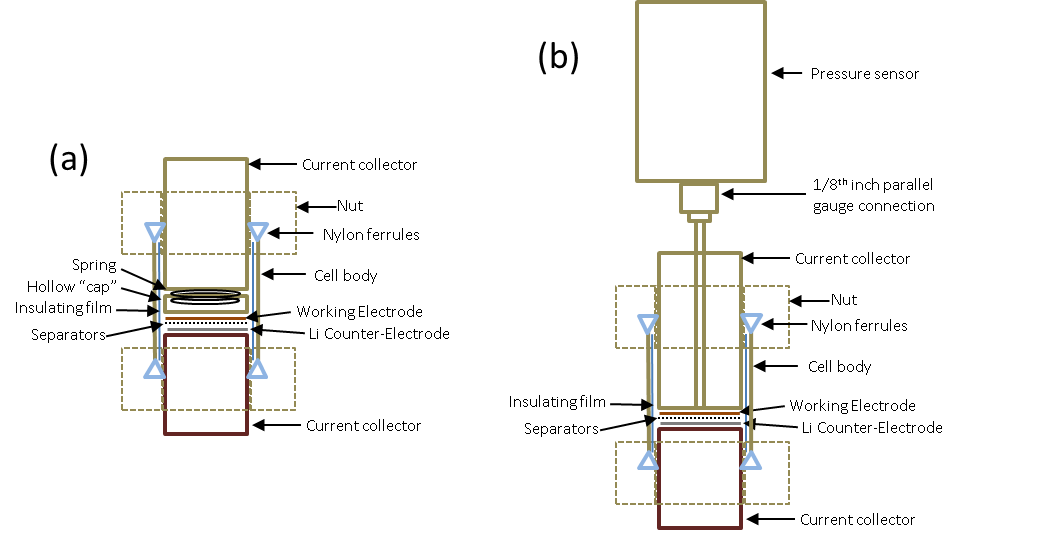


Figure 1. Standard (a) and modified Swagelok cell design for operando pressure measurements (b).

2. 2. Electrode preparation

Electrodes were made by doctor blading a thick slurry ink onto a fine stainless steel mesh (The Mesh Company, UK, woven wire mesh #500, made of 25 μm diameter wires of stainless steel 316 grade with 26 μm diameter square holes). Figure 2 shows optical images of the coated mesh. The mesh facilitates the rapid transport of gases and the transmission of pressure changes to the pressure sensor.32,45,46

(a)

(b)

(c)

Figure 2: Optical microscopy images of mesh electrodes: (a) shows the uncoated compressed mesh, (b) shows the ink deposited side of the mesh, (c) shows the underside of a coated mesh, the particles are visible through the holes of the mesh and some parts of the underside of the mesh are visibly coated in thin layers of ink. All images were taken with the same magnification.

Electrodes were made with formulations with high content of active materials, relevant for commercial applications.29,30 The LiFePO4 electrodes had a mass ratio of LiFePO4 : conductive carbon : binder of 92:4:4, and the graphite electrodes had a mass ratio of graphite : conductive carbon : binder of 95:2.5:2.5. The inks for the LiFePO4 electrodes were made with 0.107 g PVDF 5130 (Solvay), 0.107 g C65 (Timcal), 2.5 g of LiFePO4 (Tatung) and 3.7 ml NMP (99.5%, Sigma Aldrich). The inks for the graphite -electrodes were made with 0.068 g of PVDF 5130 (Solvay), 0.068 g C65 (Timcal), 2.545 g MAG graphite (Hitachi) and 6.6 ml of NMP (99.5%, Sigma Aldrich). The inks were mixed in a planetary mixer (Thinky ARE - 250, Japan) three times at 2000 rpm for 5 minutes, with 5 minute breaks in between for cooling. The doctor blading was performed using an MTI coater (MTI MSK-AFA-III) and the ink was subsequently dried in a vacuum oven at 80 °C overnight. Mesh electrodes were punched in discs of 25 mm of diamter from the dried sheet using a precision puncher (Nogami 25mm handheld precision punch, Japan). The electrodes were then compressed using a 1 inch die under 5 tonnes of pressure, corresponding to 100 MPa (Specac Manual Hydraulic Pellet Press). Compression is known to improve the adhesion and the electronic conductivity of the electrode coatings.29,30

2. 3. Cell cleaning and assembly

The current collectors and insides of the cells were carefully polished with sand paper (3M P1200 wet and dry sand paper) and then rinsed 3 times with abundant deionized water, followed by sonication in isopropanol (Sigma-Aldrich) for 10 minutes, then ethanol for 10 minutes (Sigma-Aldrich). All the cell parts were dried overnight in a vacuum oven at 80 °C, after which, they were transferred to an argon-filled glovebox. Cell parts were allowed to cool for at least 6 hours prior to assembly (this prevented degradation of the electrolyte in contact with warm cell parts and it also enabled a more stable seal of the cells). Electrodes and separators were dried under vacuum in a Büchi tube at 120 °C for at least 24 hours, and were transferred inside the Büchi tube to the glovebox without any exposure to air.

Cells were assembled with a Li electrode (25 mm diameter, 0.10 mm thick, Rockwood Lithium), two glass fibre separators (25 mm diameter, Whatman GF-F) and a working electrode (25 mm diameter) made of either LiFePO4 or graphite deposited on steel mesh, as described above. A volume of 700 μl of electrolyte LP57 (Soulbrain, MI) was added to the cell. An insulating film (0.025 mm thick, FEP electrical and chemical insulating film, RS Components) was wrapped inside the cell to prevent that the electrodes could get in electrical contact with the cell body.

2.4. Electrochemical and pressure measurements

All experiments were conducted using a VMP2 or VMP3 potentiostat (Bio-logic Science Instruments) with the cells placed inside a Memmert climactic chamber set to 25 °C. Prior to the electrochemical measurements, the cells were allowed to equilibrate for at least 12 hours, which enabled enough time for the cells to reach the temperature inside the climatic chamber. The pressure sensor (PA-33X, Keller Druck AG) also contains a temperature sensor, thus enabling monitoring the pressure and temperature of the cells. For all the experiments here reported, the variation of the cell temperature during the experiments was less than 0.2 °C. In order to compensate for temperature variations, all pressure values reported here have been corrected as follows:

Pressure (corrected) = Pressure (experimental) \* 298 K / Temperature (experimental)

However, the effect of temperature correction is very small: A comparison of the experimental and corrected values of pressure is provided in the supplementary information (section 3).

Electrochemical cycling of LiFePO4 electrodes was made at a C-rate of C/2 (where 1C corresponds to a specific current of 170 mAh g-1), between 2.8 and 4.4 V vs. Li+/Li, for 20 cycles. For the graphite electrodes, two formation cycles at C/20 were applied first, followed by 20 cycles at C/2 (where 1C corresponds to a specific current of 330 mAh g‑1), between 5 mV and 1.5 V vs. Li+/Li.

The use of a steel mesh as electrode substrate (instead of a foil) is required to facilitate the transport of gases out of the electrode,32,45,46 but produced less homogenous coatings. Still, reasonable electrochemical performance could be obtained: LiFePO4 delivered a capacity of 135 mAh g-1 at C/2, which decreased to 130 mAh g-1 after 20 cycles. Graphite delivered a capacity of 300 mAh g-1 at C/2 (after the two formation cycles), which decreased to 285 mAh g-1 after 20 cycles.

2.5. Evaluation of the total cell headspace volume

Full details of the evaluation of the total cell headspace volume when connected to the pressure sensor are provided in the supplementary information (section 2). Briefly, the evaluation of volumes was carried out by using a container of known volume, and monitoring the variation of pressure when connecting a container of unknown volume and different initial pressure.

3. Results and discussion

Figure 3 shows the results of the operando pressure monitoring of LiFePO4 vs Li half-cells during cycling at C/2. Cyclic changes in the pressure are observed to be correlated with the electrochemical cycling, with LiFePO4 oxidation (delithiation) producing an increase in pressure and FePO4 reduction (lithiation) producing a decrease in pressure. On top of the cyclic oscillations in pressure, a slow increase in pressure overtime is also observed. While the cyclic oscillations in pressure are reproducible (see a repeat experiment in the supplementary information, section 4), the slow changes in pressure overtime vary from cell to cell.



Figure 3. Operando pressure measurements of a LiFePO4 vs Li cell during C/2 cycling, using a LiFePO4 electrode with loading of 7.59 mg cm-2 deposited on steel mesh.

The analysis of the cyclic changes in pressure induced by the electrochemical cycling deserves further attention. Figure 3 shows that the same change in pressure, but with opposite sign, is observed upon application of a positive or negative current to the LiFePO4 in the Li half-cells. It is also observed that the change in pressure with time is nearly linear within each half-cycle, which implies that the change in pressure is nearly proportional to the amount of charge passed through the cell in each half-cycle. The nearly linear time dependence and the high reversibility of the cyclic pressure changes suggests that they are not due to the evolution and subsequent consumption of gases, since the evolution of gases typically starts at particular potentials that trigger gas evolution reactions and the consumption of gases would be hindered by the transport of gases to the cell headspace. In addition, it is known that the electrochemical cycling of LiFePO4 does not produce any gases: The analysis of gases evolved from LiFePO4/Li4Ti5O12 cells by operando electrochemical mass spectrometry47 and by neutron imaging48 reveals that only H2, and in very small amounts, is formed as a result of the reduction of traces of water on the Li4Ti5O12 electrode.

On the other hand, the nearly linear time dependence and reversibility of the cyclic changes in pressure could be explained by the fact that electrochemical reactions induce reversible changes in the electrodes’ volume, whose extent correlates with the amount of charge inserted in each half-cycle, and such changes in volume compress/decompress the gas in the cell headspace producing cyclic changes in pressure. However, the electrochemical reactions of lithium insertion and extraction from LiFePO4 produce small changes in volume of the crystallographic structure. XRD measurements show that the transformation of LiFePO4 to FePO4 produces a decrease in the unit cell volume of ca. 6.5%:8

LiFePO4 → FePO4 + Li+ + e-

The change in pressure in the cell associated with a change in volume of an electrode material can be calculated from:37

ΔP=P­0 ΔV/ (Vcell –ΔV) (1)

where ΔP is the change in pressure in the cell, P0 is the initial pressure, ΔV is the change in volume of the electrode material and Vcell is the total cell headspace volume (1.9 ml in the present case). Table 1 shows the results of the calculations of the changes in pressure associated with the contraction of the LiFePO4 crystallographic structure and full details of the calculations are provided in the supplementary information (section 6).

Table 1 shows that a *decrease* in pressure of -0.29 mbar is expected for the process of delithiation of LiFePO4 (positive current). However, the experimental result is that the pressure of the cell *increases*, by around 1 mbar, upon application of a positive current inducing the delithiation of LiFePO4. In order to explain the experimental result, it must be acknowledged that the delithiation of LiFePO4 at the working electrode is coupled to lithium plating on the lithium counter-electrode:

Li+ + e- →Li

Figure 4a sketches the changes in volume of the LiFePO4 and Li electrodes during cycling of the LiFePO4 vs. Li half-cells. Concomitant with the contraction of the LiFePO4 electrode during the delithiation process (positive current), the volume of the lithium counter-electrode increases as more lithium is deposited, and for the experiments in Figure 3, a change of +1.31 mbar is estimated to be associated with the lithium plating reaction (see table 1 and details of calculations in the supplementary information, section 6). Overall, the process of delithiation of LiFePO4 in a LiFePO4 vs Li half-cell is estimated to produce a total change in the cell pressure of +1.02 mbar (table 1), which is in good agreement with the experiments.

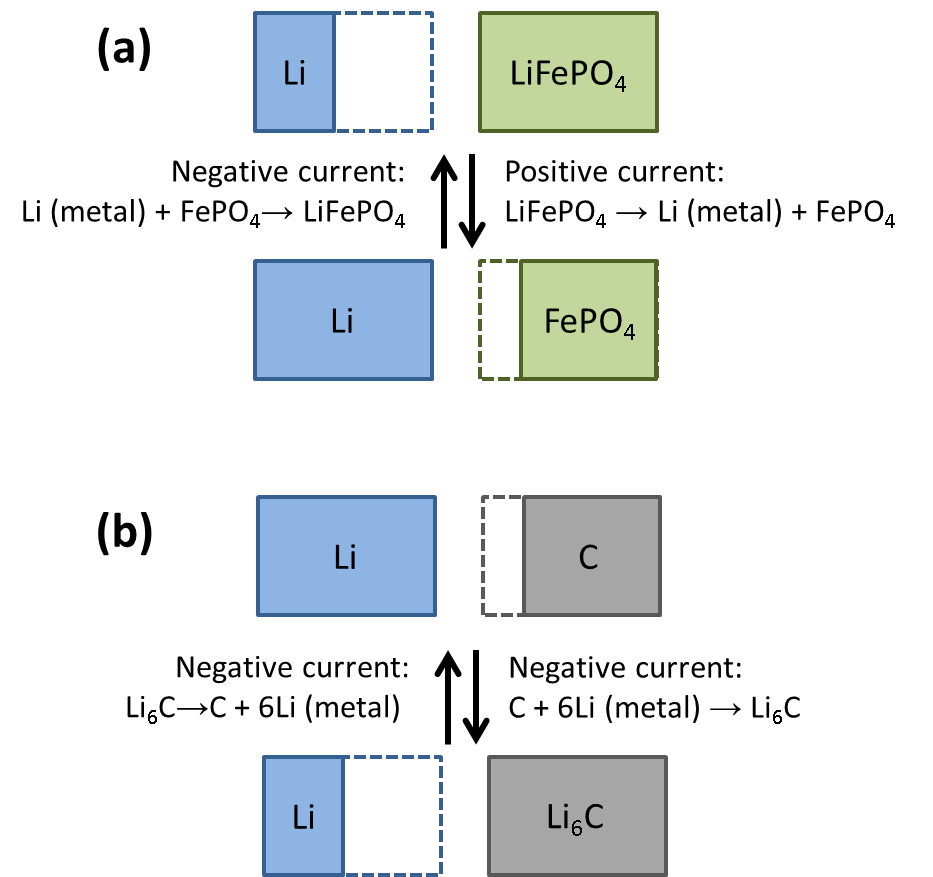


Figure 4. Sketch of the volumetric changes of electrode active materials induced by electrochemical cycling of LiFePO4 vs. Li (a) and graphite vs. Li (b) cells.

Table 1. Calculations of the pressure changes associated with volumetric changes of the electrodes’ active material induced during the electrochemical cycling (see details of calculations in the supporting information, section 6).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Cell | Working electrode reaction | Calculated change in pressure due to the working electrode reaction | Counter electrode reaction | Calculated change in pressure due to the counter electrode reaction | Calculated total change in pressure of the cell |
| LiFePO4 vs Li | LiFePO4 → FePO4 + Li+ + e- | -0.29 mbar | Li+ + e- → Li | +1.31 mbar | +1.02 mbar |
| graphite vs Li | 6C + Li+ + e- → LiC6 | +0.71 mbar | Li → Li+ + e- | -2.15 mbar | -1.44 mbar |

In conclusion, the new cell design here presented enables a high precision operando pressure monitoring of electrochemical cycling of battery materials, which can be used to follow the volumetric changes of the electrodes associated with electrochemical reactions. Very simple calculations of the expected changes in pressure, using XRD data on the structural expansion of the battery materials, produce values that are in good agreement with experiments. Closer inspection shows that the calculations provide values of the expected change in pressure of the cell that are somewhat lower than the values measured experimentally. This could be due to the fact that the changes in volume of the LiFePO4 composite electrode are compensated, at least partially, by the polymer binder. Another possible explanation is that the reaction at the Li counter electrode involves electrolyte degradation (e.g. SEI formation) in addition to the pure Li plating/stripping reactions here considered for the calculations. This could be studied in further work by using an electrode material with minimal volumetric expansion associated with lithium ion insertion/extraction reactions, such as Li4Ti5O12.49,37,9

As mentioned before, superimposed to the cyclic oscillations in pressure induced by the electrochemical cycling, the results in figure 3 also show a slow variation of pressure overtime, which amounts to ca. 6 mbar over a period of 60 hours. This slow change in pressure is attributed to the formation of a small amount of gases in side reactions. In additional experiments, it was found that small amounts of oxide residues in the cell body could cause significant build up in pressure over time, whereas careful polishing of the cell body produces a much more stable pressure (see supplementary information, section 5). Consequently, the build-up in pressure can be explained by the transformation of metal oxides into metal (oxy)fluorides induced by the decomposition of LiPF6,50,51 this reaction also forms reactive gases such as POF3 that can in turn induce the degradation of the carbonate electrolyte forming CO2.52–56 A detailed discussion of possible reaction mechanisms that can produce the observed slow change in pressure is provided in the supplementary information (section 8). Further work will investigate the use of aluminium cells, since aluminium is known to be much more stable against corrosion phenomena in LiPF6 electrolytes.57–59 However, other phenomena might also play a role in the slow change in pressure overtime observed in the present measurements. The slow build up in pressure can also be due, in part, to the reaction of the lithium electrode with trace amounts of water or other electrolyte impurities producing H2.33,60 An increase in pressure of 5 mbar is expected if all the water in the electrolyte (20 ppm) reacted to form H2 (see details in the supplementary information, section 8). Another possible origin of the build-up in pressure is the formation of CO2 via the base-catalyzed degradation of ethylene carbonate, which could be initiated by the reduction of trace amounts of water at the lithium counter electrode.61,62,32,46 This could be studied in further work by substituting the lithium electrode by an inert counter-electrode material such as charged LiFePO4.56

Figure 5 illustrates the operando pressure measurements of a graphite vs. Li half-cell during the first two formation cycles at C/20, followed by fast electrochemical cycling at C/2. A marked increase in pressure is produced during the first lithiation of graphite, which can be attributed to the formation of gases as some of the reaction products in the formation of an SEI on graphite.63–67 The change in pressure amounts to ca. 40 mbar, which corresponds, using equation (1), to a change in volume of 71 μl (see details of calculations in the supplementary information, section 7). Since the amount of graphite in the cell was 32 mg, the ratio of volume of gas evolved per mass of graphite amounts to ca. 2.2 μl mg-1. Similar results have been reported by Gasteiger and coworkers,32,33 who detected the evolution of gases by on-line electrochemical mass spectrometry in a gas volume to graphite mass ratio of ca. 2 μl mg-1 during the first lithiation of graphite SLP30 (Timcal) in cyclic voltammetry experiments (see details of calculations in the supplementary information, section 7), in good agreement with the value of 2.2 μl mg-1 obtained here for a MAG Hitachi graphite during cycling at C/20. In order to bring a deeper understanding into the mechanism of gas evolution and SEI formation on graphite, further studies could investigate the effect of the type of graphite, graphite loading, electrolyte additives and electrochemical protocol on the evolution of gases from graphite cells.



Figure 5. Operando pressure measurements of a graphite vs Li cell during the first two formation cycles at C/20, followed by C/2 cycles, using a graphite electrode with loading of 6.46 mg cm-2 deposited on steel mesh.

Figure 6 shows an enlarged view of the fast electrochemical cycling at C/2 of another graphite vs. Li half-cell. The cyclic changes in pressure induced by the electrochemical cycling are clearly visible. As shown in table 1, the cyclic pressure changes can be explained by the changes in the volume of the electrode active materials, and are dominated by the change in the lithium counter-electrode volume, see Figure 4b. The calculated changes in pressure associated to the lithium counter electrode reactions are higher in the case of graphite vs Li cells than in LiFePO4 vs Li cells because the capacity of the former cells was higher (8.2 mAh rather than 5.0 mAh, see section 6 in the supporting information), which is a consequence of the higher specific capacity of graphite compared to LiFePO4. For both types of cells (graphite vs Li and LiFePO4 vs Li), the calculations of the expected changes in pressure (table 1) are in good agreement with the experiments, and deviations can be ascribed to the fact that the Li counter electrode reactions involve side-reactions (e.g. electrolyte degradation),68–70 and the fact that the volumetric changes of the electrode active materials can be buffered by the elastic behaviour of polymeric binders or SEI coatings.71–76

In summary, the highly sensitive set-up here developed enables the detection of gases evolved as a result of electrochemical processes (for example, the SEI formation on graphite) and also enables the detection of smaller changes in pressure induced by volumetric changes of electrode materials.



Figure 6. Operando pressure measurements of a graphite vs Li cell during fast C/2 cycling (after two formation cycles at C/20), using a graphite electrode with loading of 5.59 mg cm-2 deposited on steel mesh.

4. Conclusions

We report a simple Swagelok cell design for operando pressure measurements of battery materials that has high sensitivity and enables the detection of small amounts of gases and changes in electrode volumes during electrochemical cycling. The cell is made with commercially available parts from Swagelok or other suppliers, and the only required modification is the use of a current collector with a hole and soldered to a small metal tube. Full technical details of the cell parts are provided, as well as detailed instructions of a method of evaluation of the cell headspace volume and polishing and cleaning procedures, in order to facilitate the adoption of this cell design by other research groups. Swagelok cells are commonly used in battery research laboratories and the pressure sensors are very affordable, thus this approach is ready available to most research groups and require no specialist equipment. This new cell design could be used for screening new battery active materials, since little amount of material is required to prepare the electrodes to run these experiments. The high sensitivity of this cell design also makes it very useful for the study of the stability of cell materials in contact with LiPF6-containing electrolytes: for example, the transformation of metal oxides to metal (oxy)fluorides induced by LiPF6 decomposition produces the evolution of various gaseous reaction products. The use of a Swagelok cell design also brings the advantage of versatility: for example, the cell could be easily adapted to incorporate a third electrode as a reference electrode by using a T-cell.77 This new cell design can also be used to study the kinetics of more complex reactions involving precipitation or gas evolution by, for example, the application of a sinusoidal current and analyzing the correlation between charge and pressure using electrochemical pressure impedance.78,79

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