Supporting Information

The critical role of lithium nitrate in the gas evolution of

lithium-sulfur batteries

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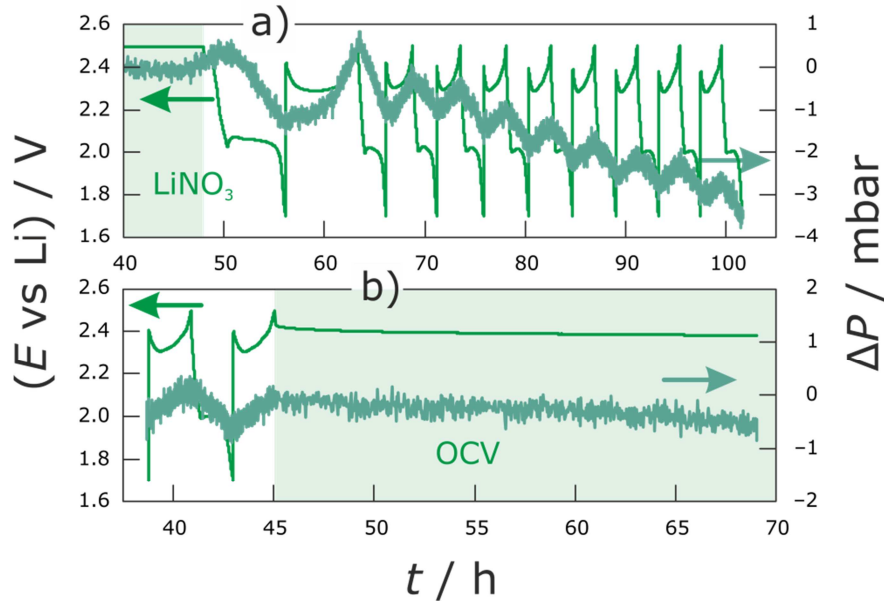
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Figure S1. Pressure trends with dependence on the charge/discharge profile for Li-S cells using diglyme/LiTFSI electrolyte with $LiNO_3$. Shaded areas represent OCV periods before and after cycling.

The effect of volume change of the lithium anode on the internal pressure change of the cell

In order to test the effect of the volume change of the lithium metal anode on the total pressure change in the cell, we have chosen a less complex and well-known system: a battery cell with a lithium anode, an NCM cathode ($LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, NCM111) and a standard electrolyte (1 mol/dm^3 $LiPF_6$ in EC:EMC 3:7 by weight). The applied setup was the same as in the case of the Li-S measurements. The capacity of the cathode material was 25 mAh. The cell was cycled with a protocol shown in Fig. S2 (top). The pressure change of the cell was monitored simultaneously (Fig. S2 (middle)).

From the current vs. time curve, we obtain the charge vs. time curve. Assuming that the charge is consumed in 100% by the deposition and dissolution of lithium (in charge and discharge cycles, respectively), *i.e.*, Coulombic efficiency of 100%, we can calculate the amount of lithium deposited and dissolved in each cycle. After determining the cell volume to be 4 ml, we can calculate the pressure change caused by the volume change of lithium (see $\Delta P_{\Delta V(Li)}$ in Fig. S2 (middle)). Because the Coulombic efficiency is not 100%, the amount of charge during the discharge process is usually lower than that in the charge cycle, therefore the increasing trend of the curve. After correcting the curve with a baseline, we obtain the "reversible" pressure, *i.e.*, the charge consumed by the reversible lithium deposition/dissolution.

A very similar trend can be identified in the measured pressure change (ΔP) vs. time curve. The reversible change is superimposed on an "irreversible" pressure change curve, originating from gas evolution in the cell from cycle to cycle. After correcting the baseline of this curve (composed of the pressure change caused by the evolving gases), we get the completely reversible contribution.

We can plot the expected pressure change from the lithium deposition/dissolution and the reversible pressure change measured in each cycle. As is seen in Fig. S2 (bottom), the two curves almost perfectly coincide. This means that the reversible curve superimposed on a monotonously increasing curve is caused by the volume change of the electrodes, in this case

that of the lithium anode. The volume of the cathode material does not change linearly with the potential (calculated from XRD) and is significantly lower than that of lithium.

We can transfer this knowledge to the more complex Li-S system and can explain the appearance of the pressure curves shown in Fig. 1:

1. In case the system contains $LiNO_3$, the gas evolution is supressed and the pressure curve shows the volume change of the lithium anode during charge (increase) and discharge (decrease).
2. Without $LiNO_3$ the evolving gases dominate the pressure curve and the fine structure caused by the volume change of lithium is hardly observable.
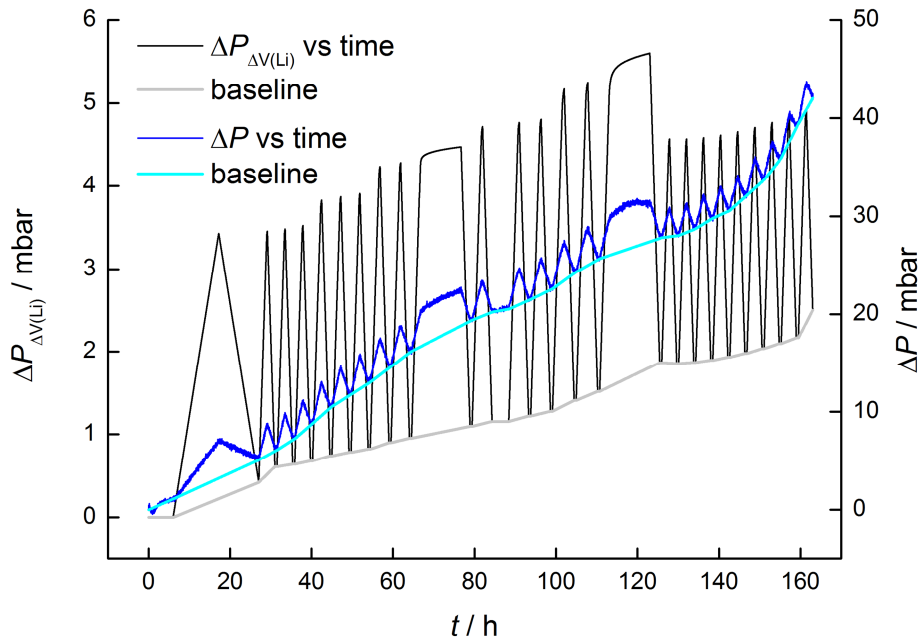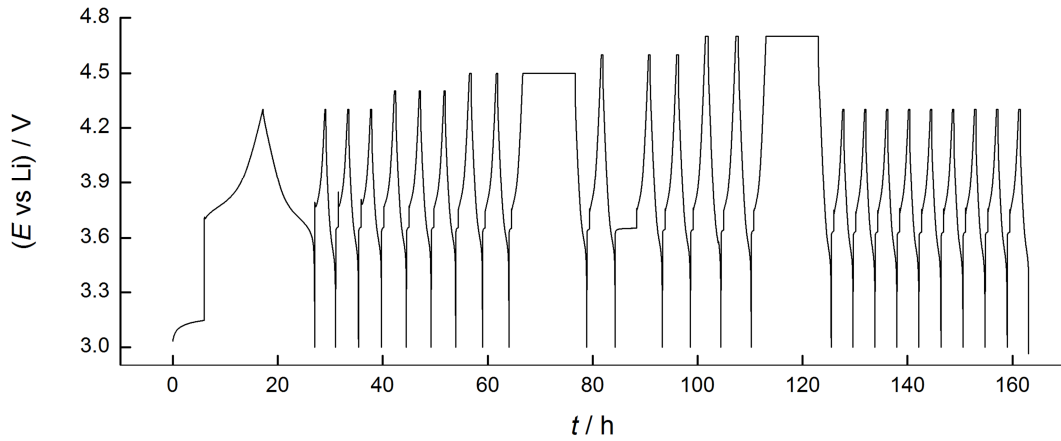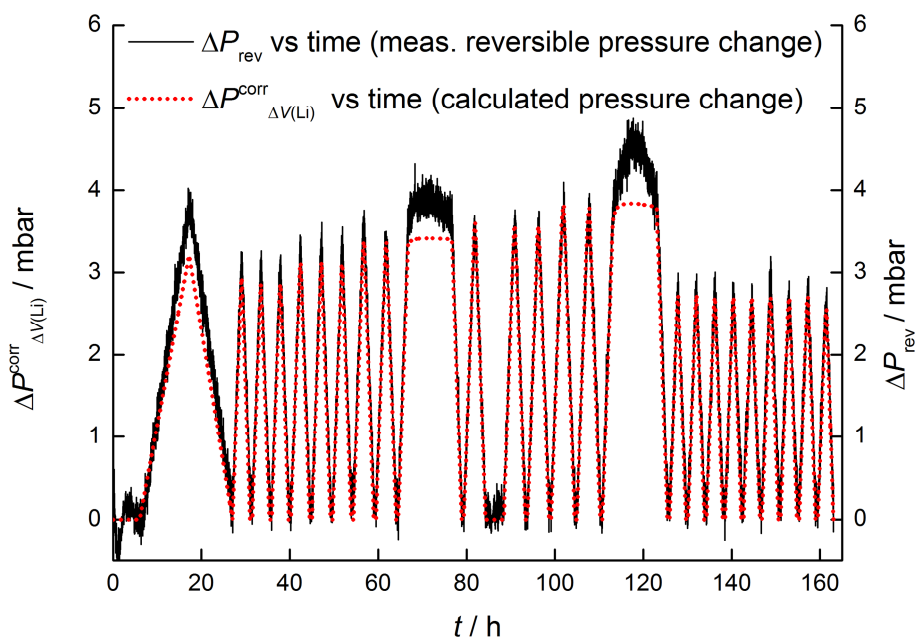
Figure S2. Pressure measurement in a Li-NCM111 cell. (top) Applied potential program. (middle) Calculated pressure change caused by lithium deposition and dissolution together with the measured pressure change curve. (bottom) Baseline corrected curves plotted together.

Gas evolution in symmetric Li-Li cells

In order to gain insight into the origin of gases, experiments in symmetric Li-Li cells have been carried out (Fig. S3). The same electrolytes (either 1 mol/dm^3 LiTFSI in diglyme or 0.325 mol/dm^3 LiTFSI and 0.675 mol/dm^3 LiNO$_3$ in diglyme) and the same current densities during charge/discharge as in the Li-S system have been applied in these cells.

In either case, unambiguous trends between the gas evolution and electrochemical cycling of the cells can be hardly observed. However, it is obvious that more gases are generated in the cell containing no LiNO$_3$. Especially the presence of H$_2$ and CH$_4$ is clear. This agrees well with our former observations. CH$_4$ can be clearly identified even with the less sensitive DEIRS (IR spectroscopy). For the cell containing LiNO$_3$, no CH$_4$ is observed in the IR spectrum. The other gases show also almost no trend, which seems to justify Eqs. 1-3 in the manuscript: the formation of gaseous N$_2$ and N$_2$O requires the presence of sulfur or sulfides (Eq. 2).
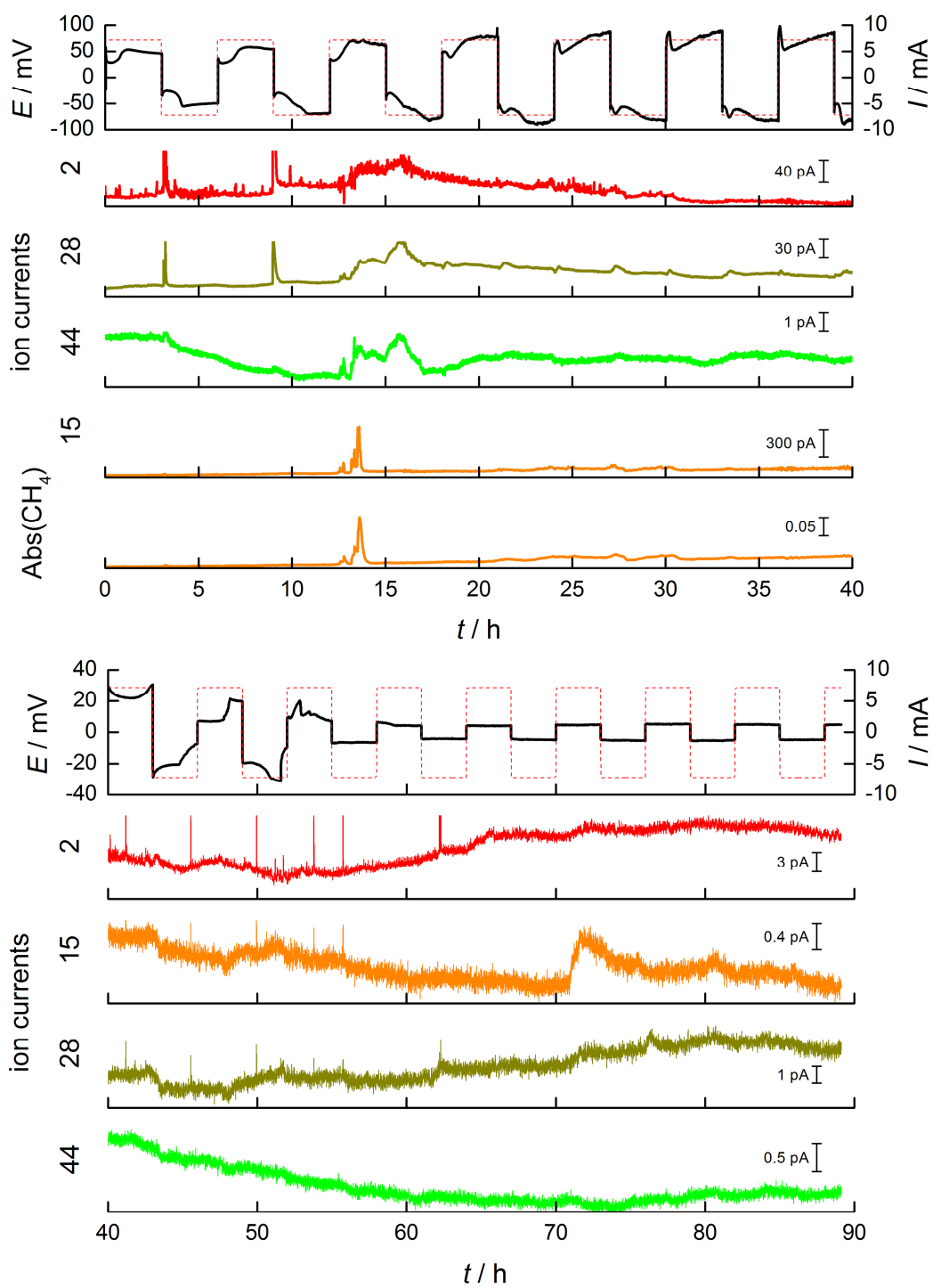
Figure S3. DEMS-DEIRS measurements of symmetric Li-Li cells without (top) and with (bottom) LiNO$_3$ additive.