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The impact of electrolyte additives determined using isothermal microcalorimetry

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The use of electrolyte additives in lithium ion batteries can extend cycle life, increase coulombic efficiency, and reduce parasitic reactions. Here, the technique of high resolution isothermal microcalorimetry [1] is used to investigate the effect of the additive vinylene carbonate (VC). By comparing the heat flow of cells that vary only in VC concentration during cycling and open circuit conditions, the effect of the additive on the parasitic heat during the entire potential range is obtained in a short, simple experiment. A TA instruments TAM III isothermal calorimeter equipped with 12 microcalorimeters was used for these measurements. The accuracy of the microcalorimeter used (< ±1 μW) allows for a highly sensitive differentiation between cells.

Figure 1a shows the heat flow versus voltage for four machine-made 225 mAh $LiCoO_2$ (LCO)/graphite pouch cells cycling at 10 mA (C/22.5) and 40°C with increasing amounts of VC. At this rate, the contributions of entropy and polarization to the total heat flow are nearly identical between cells, such that any differences in measured heat are attributable to differences in parasitic heat.

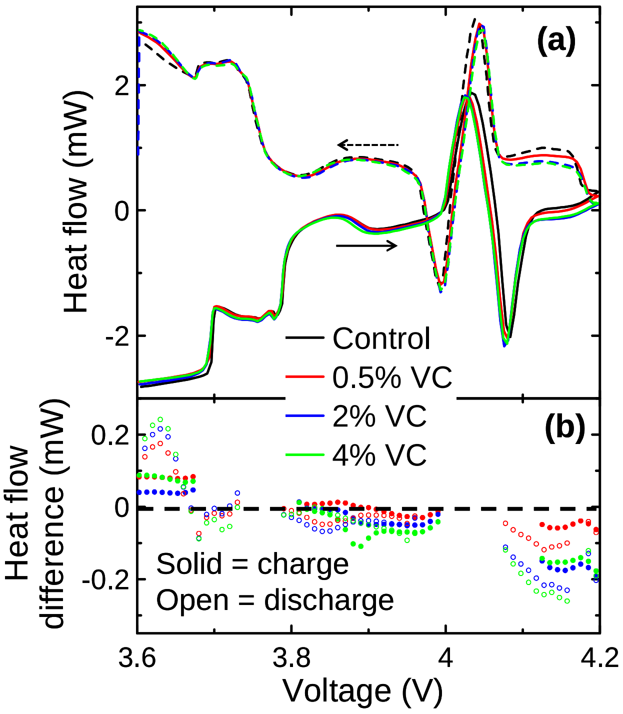

Figure 1. (a) Heat flow as a function of voltage for LCO/graphite pouch cells containing increasing amounts of VC charged (solid) and discharged (dash) at C/22.5 and at 40°C. (b) Difference between the heat flow of VC-containing cells and the heat flow of the control cell.

Figure 1b shows the difference obtained by subtracting the heat flow of the control cell (no VC) from the heat flow of the VC-containing cells as a function of potential. This difference is a good measure of the reduction in parasitic heat due to the addition of an additive. Figure 1b shows that even a small amount of VC reduces the parasitic heat in LCO/graphite cells above 3.9 V. The effect of VC at all voltage ranges and during subsequent cycles will be discussed in greater detail.

Figure 2a shows the evolution of the heat flow of the same set of cells as they are left at open circuit conditions after being charged to 4.2 V. Since no current is applied to the cells, open circuit heat flow measurements provide a direct measure of the heat flow due to parasitic reactions. A pronounced reduction in parasitic heat is seen with increasing amounts of VC, in qualitative agreement with the results shown in Figure 1. Figure 2b shows the corresponding voltage drop during the open circuit measurement.

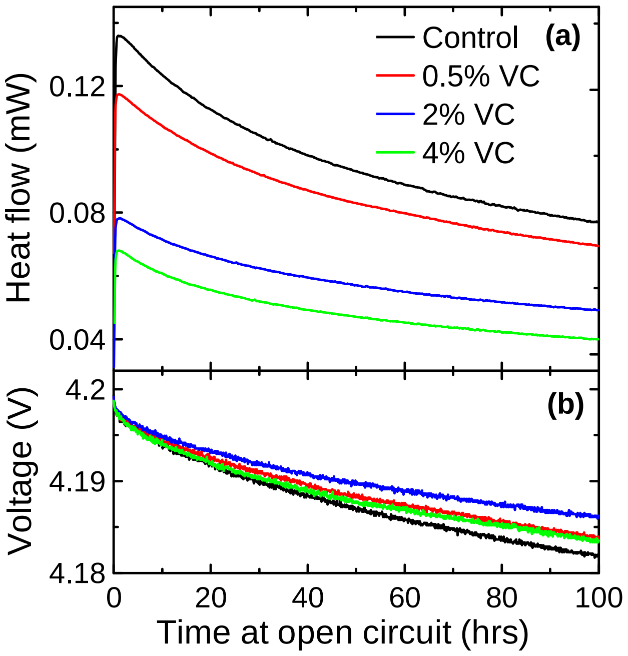

Figure 2. (a) Heat flow versus time for LCO/graphite pouch cells with increasing amounts of VC at open circuit conditions at 40°C after being charged to 4.2 V. (b) Voltage versus time during the open circuit measurements.

The above results clearly demonstrate that isothermal microcalorimetry is an extremely powerful technique able to measure the potential range over which any additive or additive combination is most effective with quick and simple experiments. This in turn will help efforts to understand electrolyte additives. Machine–made 225 mAh pouch cells are exceptionally convenient for these studies as they are nominally identical (except for the electrolyte) and because they evolve heat that is two to three orders of magnitude above the noise level of the instrument.

Data will also be presented showing the impact of a variety of additives in $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) /graphite pouch cells.

References

[1] L. J. Krause, L. D. Jensen, and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A937–A943 (2012).