# Observation and Mechanism of Anomalous Local Potentials during Charging of Lithium Ion Cells

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**Background.** Chemical reaction products are visually observed in lithium ion cells that would not be expected in the normal range of electrode potentials during cell formation and cycling (i.e., from about 3 to 0.1 V vs Li for carbon negative electrodes and 3 to 4.2 V for $LiCoO_2$ positive electrodes). For example, metallic lithium at certain edges or turns of the negative electrode is commonly reported. Metallic lithium indicates $Li^+$ reduction at potentials $\leq 0$ V. In addition to this phenomenon, we have observed polyparaphenylene (PPP) at interconnects of the positive electrode. PPP forms from oxidation of biphenyl (BP) [1], an additive used for overcharge protection, at about 4.6 V. This paper reports on the observation of the latter product and provides a mechanistic explanation that may be extended by analogy to explain lithium deposition and other reactions.

**Experiment.** Coiled prismatic lithium ion cells were fabricated using conventional electrode coating methods and mass loadings [2]. The active electrode materials were $LiCoO_2$ and graphitized MCMB. The electrolyte consisted of 1 M $LiPF_6$ in a mixture of organic carbonates, with 2.4 wt% BP and a proprietary anti-fade additive. Hermetic cells were made in stainless steel cans and contained a Li reference electrode in the headspace (position “HS”). Non-hermetic cells were made with the same geometry in a polymer/glass vessel, but with three reference electrodes. Two were placed between the positive and negative electrodes; one was located near the midpoint along the electrode length (position “MD”), and the other was placed at the center of the jelly roll, in a region where there active MCMB opposed the bare Al positive current collector (position “AL”). The third reference was placed just outside the outer wrap of the coil (adjacent the bare Cu foil negative current collector, position “CU”). Potentials were monitored during charging (C/10 rate) at 37 °C to a cell voltage of 4.1 V.

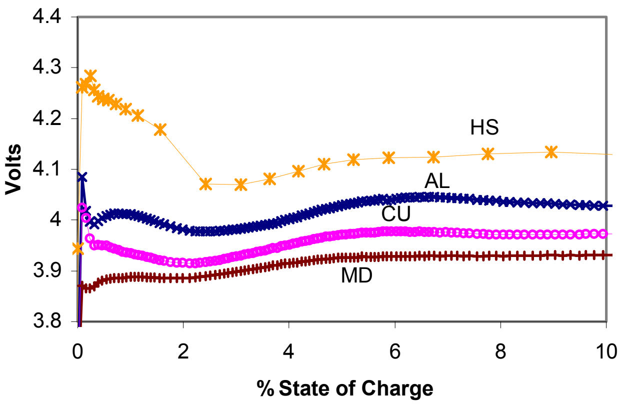
**Results and Discussion.** Destructive analysis of cells after initial charging indicates the presence of a dark brown tar-like residue on the positive tab, feedthrough pin, the uncoated portion of the Al current collector, and the adjacent separator. From cyclic voltammetry, we have found that such material is associated with an anodic peak associated with BP, that onsets at about 4.6 V, close to the literature value for PPP formation [1].

The potential of the positive electrode versus the various reference electrodes at the beginning of the first charge cycle is shown in Figure 1. Curve MD represents the average potential of the positive electrode, because it nearly perfectly overlays the curve obtained for $LiCoO_2$ versus Li in coin cells (data not shown). At early times, curve HS quickly rises to nearly 4.3 V, which is about 0.4 V above curve MD. Curves AL and CU fall between the other two. The 0.4 V difference between HS and MD exceeds that which could be explained by ohmic drops in the current collector or by concentration-induced shifts in the reference potential. Rather, the large potential difference is consistent with an IR-induced potential gradient in the electrolyte, in a direction parallel to the plane of the electrodes. Although the maximum measured value of 4.3 V is about 0.3 V lower than the potential for generation of PPP, the PPP was empirically observed. This is strong evidence that potentials at or above 4.6 V existed in certain locations and possibly over short timeframes, but were not measured due to limitations of the reference electrodes, e.g., position, nonzero size and time resolution.

We interpret the electrolyte potential gradient as originating from a local galvanic cell near the edges of the negative electrode, driven by a [Li] gradient within the MCMB. For the cells studied, the MCMB active negative material overlapped the edges of the $LiCoO_2$ active positive material by about 1 mm at all electrode edges (per conventional practice), except for near the innermost edge, where the overlap was more than 10 mm. During charging, the regions of unopposed MCMB uptake Li more slowly than the “bulk” of the MCMB, and the overlap and bulk zones therefore have different potentials. To illustrate this, consider that early in the first charge cycle, a change in state of charge of MCMB from 0 to 1% results in a shift in potential from about 3 to less than 1 V (a net drop of > 2 V). Such a 1% difference in lithiation (or greater) is likely to exist between the bulk and the overlap zones, due to a difference in relative proximity to the $LiCoO_2$. The resulting potential drop along the MCMB results in a galvanic current between the two zones, causing an IR drop in the electrolyte. This effectively increases the potential of the positive electrode relative to the electrolyte in the overlap region, resulting in oxidation of the BP to PPP.

The mechanism proposed here explains the presence of PPP, and an analogous process can explain lithium plating on the negative electrode. Together, these provide a basis for the existence of local electrode potentials significantly above or below the conventionally expected values, possibly providing insight for the interpretation of other reactions, e.g., electrolyte decomposition, SEI formation and current collector corrosion.

**Figure 1.** Positive electrode potential vs references HS, AL, CU and MD, during the first 10% of charge



**References**

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[1] Lee, et al, *J. Electrochem. Soc.*, **148**, D139 (2001).

[2] Section 35.3 in Linden and Reddy, Handbook of Batteries, 3rd edition, McGraw-Hill, 2002.