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Exploring Li distribution in Li-ion batteries with FIB-SEM and TOF-SIMS

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Differences in reaction rates across an electrode in lithium (Li) ion batteries can lead to inhomogeneous degradation of electrochemically active particles, especially at high cycling rates. A number of studies have explored such inhomogeneous degradation [1-3]. Other studies have focused on Li distribution [4,5], including the use of FIB-SEM with EDX and TOF-SIMS to identify Li-ion "trapping" sites at grain boundaries and particle-matrix interfaces in cathode particles in discharged samples [6]. However, the measurement of Li distribution across an entire electrode has proved elusive.

In this work, the global and local distribution of Li in an aged cathode from a discharged cell was measured using a TESCAN FERA Xe plasma FIB-SEM configured with TOFWERK Time-of-flight secondary ion mass spectrometer (TOF-SIMS). TOF-SIMS is among the few approaches that can provide information regarding the spatial distribution of Li. Measurements focused on the cathode of an NCM523/graphite full cell that underwent 400, 3.0-4.4 V cycles at 30°C. After cycling, this cell exhibited a 40% loss of capacity as well as a significant rise in impedance entirely attributable to the positive electrode. The high current Xe plasma FIB facilitated preparation of large area cross-sections that allowed both global and local measurement of Li in the positive electrode using TOF-SIMS.

Figure 1 shows the top projection SIMS image corresponding to ^{7}Li together with the secondary ion image of the electrode cross-section. Variations in intensity from particle to particle as well as within individual cathode particles indicate variations in Li content. The regions closest to the separation membrane appear to have a higher overall Li content than regions closer to the current collector. Mass spectra, shown in Figure 2, confirm this observation. The summed spectrum for 4 particles nearest the separation membrane shows a significantly higher level of Li compared to the particles closest to the current collector while Mn content is the same. Fig. 3a shows the distribution of ^{7}Li in a single cathode particle. This image reveals a significant enhancement of Li at the periphery of the particle and at grain boundaries within the particle. Fig. 3b shows the distribution of ^{19}F in a different nearby particle. Similar to Li, there is a significant level of F present at the periphery of the particle and, importantly, along grain boundaries within the particle. Since the $LiPF_6$-based electrolyte is the source for F, this observation supports a mechanism in which particle grain boundaries "crack" during cycling, allowing electrolyte to penetrate the boundaries [7]. However, the enhanced levels of Li in these regions together with signatures in the TOF-SIMS spectra for Li-F phases (not shown) further suggests that reaction phases form at these interfaces

These results suggest heterogeneous Li distribution and reaction phases play a role in limiting Li mobility and lead to reduced performance and life of lithium-ion cells.

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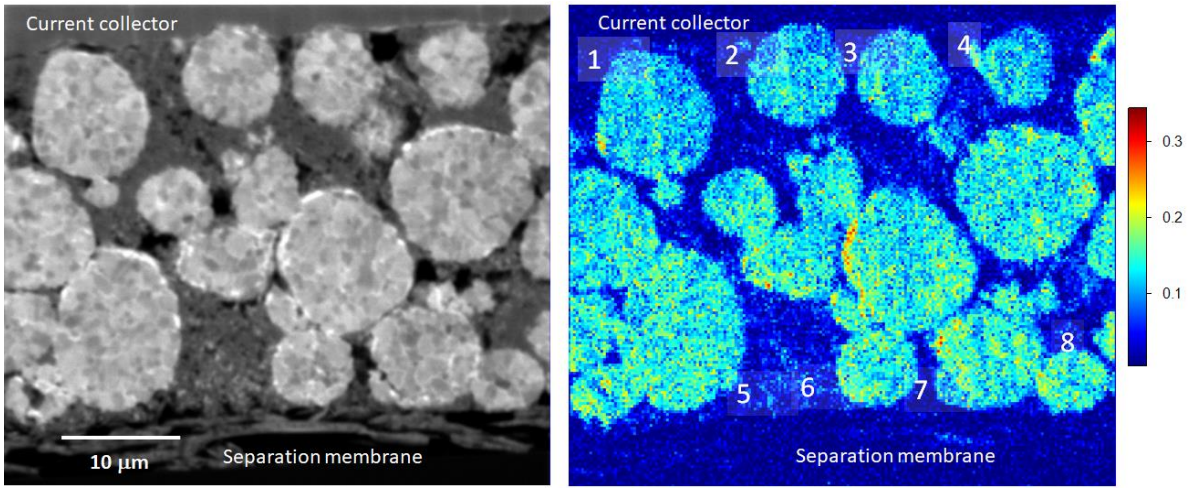

Figure 1. (a) Ion image and (b) top projection SIMS image for mass 7 [Li] of the entire electrode cross-section.

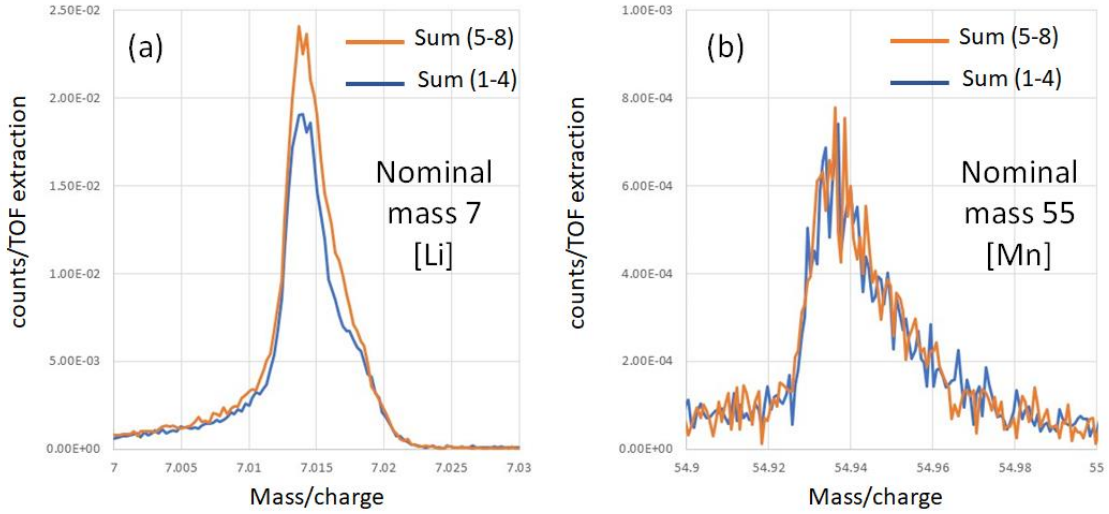

Figure 2. Mass spectra, summed as marked in Fig 1 for representative particles nearest the current collector (particles 1-4, blue) and separator (particles 5-8, orange), (a) for mass 7 [Li] and (b) for mass 55 [Mn].

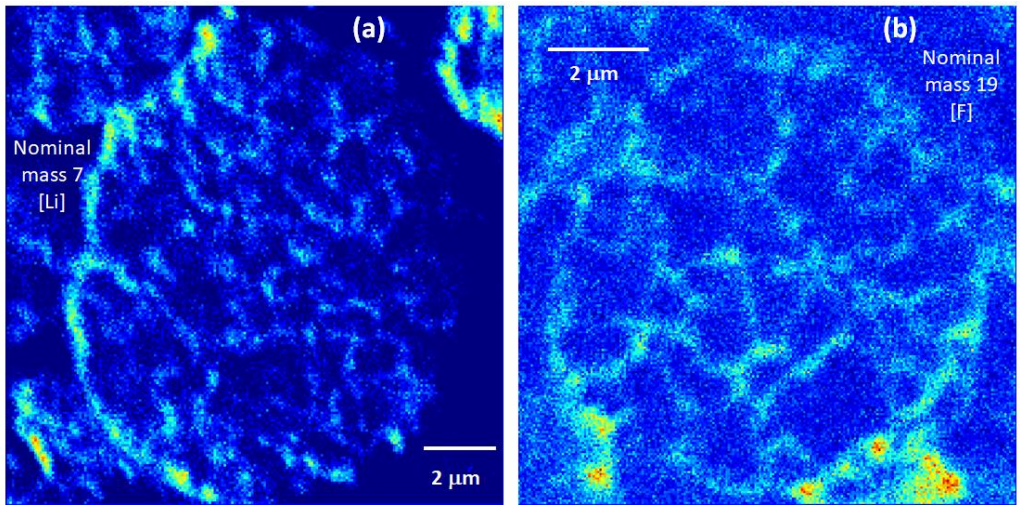

Figure 3. Top projection SIMS images from single cathode particles (a) for nominal mass 7 corresponding to Li and (b) for nominal mass 19 corresponding to F.

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