Morphological Peculiarities from Lithium Plating and Stripping

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Enabling metallic-Li negative electrodes is motivated by a significant increase of energy density, both gravimetric and volumetric (Fig. 1), despite the excess of metallic Li accounted to ensure a stable potential. The projected gain in energy density for post-Li-ion batteries with metallic Li is twice than that possible to achieve with graphite, whereas with current and potential positive electrodes of Li-ion batteries it is about 30 % [1]. However, Li-metal as an anode is prone to dendritic growth and, therefore, is considered an unsafe option. It has been under investigation since early 1970s and the interest declined with the invention of Li-ion battery technology, which was considered safer alternative. However, recently interest in the metallic Li has been again on a sharp rise [2]. There is still insufficient fundamental understanding about the fundamental principles, governing electrochemical lithium plating/stripping, which often results in dendrite growth, electrolyte consumption, other undesired effects. [3]

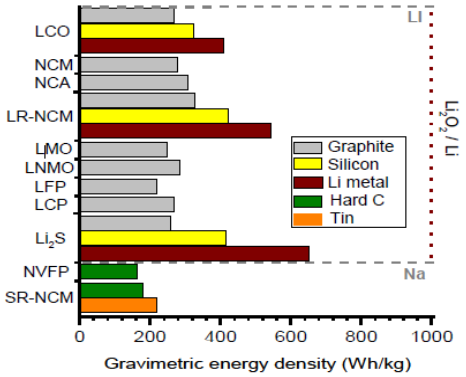

Figure 1. Gravimetric and volumetric energy densities of various positive electrodes paired with negative electrodes [1]. Energy density vs metallic Li electrode is denoted in bordeaux.

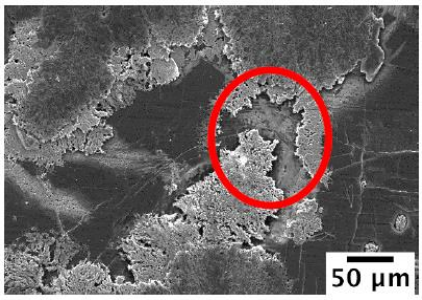

Figure 2. Li deposits after two platings and one stripping in-between them. The red ellipse highlights an area where 'dead' Li surrounds empty space, where previously active Li has been.

The present study aims to gain a comprehensive fundamental understanding of metallic-Li behaviour upon plating/stripping. As a first step, we performed post-mortem SEM analysis during the first two cycles in various electrolytes, in addition to studying the cycling performance in Li–Cu and symmetric Li–Li cells. Our post-mortem SEM study revealed that Li plates sporadically, where some of the regions are preferred for plating, despite 'dead' Li agglomeration on those particular spots, while the other regions are free of Li deposits (Fig. 2). The most interesting morphological changes are obtained during the initial stages of stripping and plating.

References

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