The crucial role of local charge fluctuations in dendrite growth

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Dissipation and fluctuations are intimately related, so in a certain sense this talk complements the reports on dissipation and friction presented at this workshop.

The surface tension of an electrode is highest at the potential of zero charge (pzc). Therefore surface fluctuations are lowest at the pzc, and increase as the electrode is charged. On an uneven surface, charge is not distributed equally, but accumulates at the tips of profusions. This suggests the following mechanism for the growth of dendrites during metal deposition.

Dendrites form when the metal cations are deposited on a negatively charged surface, i.e. below the pzc. In this case, any protrusion that forms during the deposition acquires a high negative charge density, which attracts more cations, and thus induces further growth at tip. Eventually, this leads to the formation of dendrites. In order to estimate the magnitude of this effect, we have performed calculations for model tips on a negatively charged electrode surface using a tight binding method based on density functional theory (DFTB). Even a small average excess charge on the electrode leads to a high accumulation of charge at a tip and a strong field, which directs the metal cations in the solution towards the tip.

When the local excess charge at a tip becomes too high, it becomes unstable and breaks off. This suggests a mechanism for the formation of dead lithium in batteries.

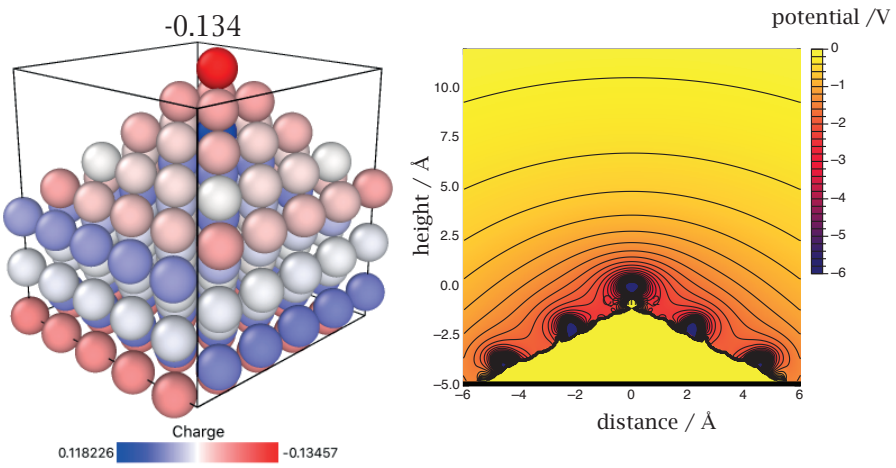

Figure 1: Charge distribution on a pyramidal tip for a Li electrode with an excess charge of $\sigma = -2.9 \times 10^{-2}\mathrm{C\ m^{-2}}$ (left) and electrostatic potential contours (right) when the tip is in contact with a medium obeying the linear Poisson-Boltzmann equation with a Debey length of 10 Å.

A brief survey of experiments shows that indeed all metals whose deposition potential lies below the pzc are prone to dendrite formation; this applies particularly to the alkali metals. In contrast, metals like copper or silver, whose deposition potential lies above the pzc, generally do not form dendrites. On such metals, dendrites can form when the applied overpotential is so high that the electrode potential lies below the pzc.

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