Fig. 1. LiF formation. On graphite, LiF is produced slowly and forms clusters with gaps between them. On a catalytically active electrode such as gold, LiF is produced at much higher rates and forms passivating films.

Lithium ion Batteries

Catalysing surface film formation

The solid electrolyte interphase which forms on graphite anodes plays a vital role in the performance of lithium ion batteries. Now research shows that the formation of lithium fluoride deposits — one of the main components of the solid electrolyte interphase — is strongly influenced by the electrocatalytic activity of the anode.

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Lithium ion batteries provide energy storage for portable electronics, electrified transport, and the electricity grid of the future. They only tend make it into the news when new breakthroughs in the amount of energy they can store (driving range) or their ability to fast-charge seem in reach. Those usually result from improvements of the active electrode materials, which in their bulk host the lithium ions in the charged/discharged state. Now, writing in *Nature Catalysis*, Strmcnik and co-workers demonstrate that the surfaces of the active materials deserve similar attention as their bulk: in contact with the organic electrolyte, they act as catalysts for highly important side reactions. And this catalytic effect strongly varies with structure and chemistry of those surfaces.

The authors focus on side reactions at the negative electrode, which in commercial lithium ion batteries (LIBs) consists of graphite powder. Graphite-based electrodes were the key invention that

allowed commercialization of rechargeable lithium-based batteries in the early 1990s (after two failed attempts using lithium metal foil that ended in re-call actions due to safety concerns)[1]. Driven by an external voltage, lithium ions leave the positive electrode (typically a transition-metal oxide as a host-structure) and move into the negatively polarized graphite electrode during cell charging. During discharge, the reverse process occurs spontaneously, and the re-intercalation of lithium into the positive electrode comes with the external electron current that powers a phone or a car. The negative electrode would not survive more than a few charge/discharge cycles if it was not protected by the Solid Electrolyte Interphase (SEI), which is permeable to lithium ions but blocks other electrolyte/solvent components from entering and destroying the graphite structure.

Despite its importance, this SEI is not a rationally designed material with tailored composition and structure. Instead, a good portion of experimental luck helped discover that certain organic-solvent based electrolytes decompose into a film that does this job. Soon, a few additives were discovered that helped improve and stabilize the SEI over longer terms[2]. Nowadays, the initial so-called formation cycles are a fixed element in LIB manufacturing, and they typically involve at least one slow and controlled charge/discharge cycle that leads to a reproducible and reliable SEI at the negative electrode. While well established, the formation process largely relies on empirical findings and experience, whereas the SEI's actual structure and composition are only known in fragments.

Numerous spectroscopic analyses of SEI films formed on graphite surfaces revealed carbonates and LiF as two key components[2], which are the two species studied in the current work. It is widely accepted that their production must involve electrochemical reduction reactions of solvent / electrolyte components. Surprisingly, those reactions were so far never tested for their response to catalytic acceleration via the underlying electrode surface. This is the approach of this paper.

Starting with the assumption that LiF-formation $2\ HF + 2\ Li^+ + 2e^- \rightarrow H_2 + 2\ LiF$ involves a step $HF + e^- \rightarrow H_{ad} + F^-$, they argue that this is not too different from $2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$, which

involves a step $H_2O + e^- \rightarrow H_{ad} + OH^-$, i.e., both involve surface-attached (adsorbed) hydrogen atoms H_{ad}. Thus, they compare LiF formation in organic electrolyte to the better understood hydrogen evolution in alkaline water-based electrolyte. Comparing the close-packed (111) surfaces of Cu, Au, Pt, and Ir, they find increasing electrocatalytic activities in this very order for both reactions. This can be rationalized via a reaction mechanism that considers how strongly H-atoms (and Li-atoms) are bound as intermediates to the underlying surface. Their attachment must be neither too weak nor too strong (Sabatier principle): otherwise, a surface will either not attract any intermediates, hence not influencing the reaction, or it wouldn't release them again, hence hindering subsequent reaction steps.

Given that none of the four metals (Cu, Au, Pt, Ir) would be suitable as negative electrode in an LIB, their study may first look like a pure ivory tower experiment. However, their finding that the choice of metal has such a strong influence on LiF-forming side reactions justifies all efforts and highlights that catalytic mechanisms must be taken into account. For (catalytically rather inactive) carbon electrodes, this means that the smallest structural modification could make all the difference. The latter is indeed demonstrated in a comparison of three different carbon model electrodes: for a given potential, LiF formation occurs at lower rates at the (rather smooth) basal plane of highly oriented pyrolytic graphite (HOPG) than it does at edge-exposes HOPG with its many defects. Even lower rates are achieved at a multi-layer graphene film deposited on Pt, reflecting that this surface exposes even fewer catalytically active sites. This could also explain why the multi-layer graphene electrode does not seem to decompose solvent molecules into carbonate species, whereas the two HOPG electrodes do.

The different chemical properties of the tested model electrodes not only imply different performances as catalysts, but also different affinities to the films formed by the products. More specifically, the LiF films formed on the metal surfaces are rather smooth and compact, whereas the films formed on the carbon surfaces see more rough and open. This is analogous to the way a

single layer of graphene on a metal surface will cause metal deposits on top of it to form arrays of clusters rather than smooth films[3]. This difference is also reflected in the way these films are passivating the surface: only on the metal surfaces does the LiF film saturate and block its own further growth, whereas the more open films on the carbon electrodes reduce but do not totally supress the ongoing conversion of HF to LiF.

Apart from details of the catalytic surface effects and the resulting films, the article provides a birds-eye view of the overall mechanism and supply chain of the side reactions. Firstly, HF is an intermediate product, formed by reaction of H_2O impurities with $LiPF_6$ (the Li-containing salt in the electrolyte): $LiPF_6 \leftrightarrow LiF + PF_5$ and $H_2O + PF_5 \rightarrow 2HF + POF_3$, i.e., 1 mole of water forms 2 moles of HF. Secondly, the further conversion of HF to LiF is an electrochemical one and not the result of a chemical reaction with surface carbonates as was previously assumed.

In summary, the authors deserve credit for transferring insights and methods from fuel cell and electrolysis research – where interfacial electrochemistry governs the main energy-related reaction steps – over to lithium ion batteries, where interface reactions are only involved in SEI formation and other side reactions. The importance of the SEI for battery performance and of any side reactions for battery lifetime certainly justifies the efforts. The demonstrated success of using well-defined surfaces of metal single crystals and graphite/graphene, in combination with spectrometric methods probing reaction products in-situ and ex-situ will hopefully inspire further studies of that type in the near future. Those should include more complex surfaces with more subtle variations of the type and density of reactive sites[4], including the fabrication of thin-film transition metal oxides[5] as model systems to study side reactions at the positive electrode.

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