## **■** LITHIUM-ION BATTERIES

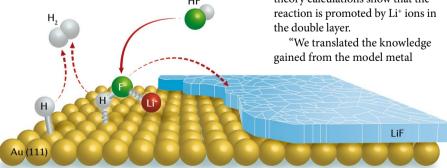
## Interrogating the interphase

Our approach is to translate the complex and undefined environment of a Li-ion battery to a well-defined one in which all the components of the electrochemical interface are known



The performance of Li-ion batteries is inherently linked to the formation of a solid electrolyte interphase (SEI) on the graphite anode. In Li-ion batteries with LiPF<sub>e</sub>-containing organic carbonate electrolytes. LiF is an ever-present component of the SEI. However, despite the importance of the SEI, the underlying mechanisms of formation of its individual constituents are poorly understood. Now, reporting in Nature Catalysis, Dusan Strmcnik, Ian Rossmeisl and co-workers show that the formation of the SEI involves the electrolysis of HF — a common impurity in the electrolyte — to form LiF and H<sub>2</sub>. Moreover, the team reveal that the anode material has a direct effect on the morphology, and thus permeability, of the SEI.

Although undesirable, HF is ubiquitous in LiPF $_6$ -based electrolytes and forms through the reaction of LiPF $_6$  with trace amounts of H $_2$ O. To establish the effect of HF concentration, [HF], on the electrochemistry at an anode, the team developed a methodology for measuring [HF] in organic electrolytes. It then becomes possible to accurately control [HF] by careful addition of H $_2$ O to the LiPF $_6$ /organic carbonate electrolyte.



Credit: Adapted from Strmcnik, D. et al. (2018), Macmillan Publishers Limited

Studying SEI formation is challenging owing to the difficulties in elucidating chemical and electrochemical transformations at the graphite/organic electrolyte interface. "Our approach is to translate the complex and undefined environment of a Li-ion battery to a well-defined one in which all the components of the electrochemical interface are known and can be controlled," says Strmcnik. The team start by monitoring the hydrogen evolution reaction on surfaces of model systems — well-defined metal single crystals, including Au(111) and Pt(111) — in the LiPF<sub>c</sub>/organic electrolyte with a [HF] of 30 ppm. During the reaction, polarization curves indicate the formation of a passivating layer, which was revealed to be a compact film predominantly composed of LiF. The effects of the rotation rate and [HF] on the current density versus potential curves were established using a rotating disk electrode: increasing either the rotation rate or [HF] leads to an increase in the current density. Overall, the results suggest that HF is electrocatalytically reduced at the metal surfaces to produce H2 gas and LiF, which precipitates as a solid film. Interestingly, density functional theory calculations show that the

systems to carbon-based materials, ranging from graphene-modified Pt(111) to highly ordered pyrolytic graphites and finally to real graphite anodes," explains Strmcnik. As well as differences in reactivity at the metal and carbon-based surfaces, the researchers report that the morphology of the LiF film is influenced by the substrate material — compact films form on metal single crystals whereas highly porous and granular films form on graphene and graphite surfaces. Moreover, in a working battery cell configuration, on-line electrochemical mass spectrometry confirms the evolution of H<sub>2</sub> at the graphite electrode during the reaction, with the amount produced being linearly proportional to [HF]. "Although the chemistry behind LiF formation does not change from model to real systems," argues Strmcnik, "the differences in the abundance of HF relative to the electrode surface area between the real battery and laboratory cell can significantly affect the composition of the SEI."

This work provides some of the first experimental evidence to suggest that the formation of LiF involves the electroreduction of HF and is an important step towards unravelling the complexity of SEI formation. The team now aim to further establish the link between LiF formation and the performance of Li-ion batteries and to use this knowledge to develop new battery technologies.

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Electrocatalytic transformation of HF impurity to
H<sub>2</sub> and LiF in lithium-ion batteries. *Nat. Catal.* 1,
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