

**Reaction of Lithium With Electrode Reactants
Containing Hydrogen or Water**

Robert A. Huggins

Faculty of Engineering
University of Kiel
Kaiserstr. 2
D-24143 Kiel
Germany

When present in electrochemically interesting materials, hydrogen is generally in the form of protons. Due to the very stringent requirements for local electroneutrality, changes in the composition of solids involves the introduction or deletion of neutral combinations of species. Thus if hydrogen is added in the form of protons, the charge balance requirement can be accomplished by the co-addition of either electronic or ionic species, i.e. either by the introduction of extra electrons or the introduction of negatively charged ionic species, such as O^{2-} ions. In the latter case this is tantamount to the addition of water to the crystal structure.

There are several different mechanisms whereby hydrogen can be introduced into solids. This can be driven chemically, for example, by ion exchange with an adjacent phase. Alternatively, it can result from reaction with water via the mechanism first discussed by Stotz and Wagner [1], in which both hydrogen and oxygen enter the solid. In this case there must be both mechanisms for the transport of both hydrogen and oxygen species within the crystal structure, and places for them to go. Hydrogen can readily enter as mobile interstitial protons. The oxygen enters the structure as oxide ions, and they must be able to move through, and occupy, pre-existing oxide ion vacancies. Thus this mechanism is only available to materials that have significant concentrations of mobile oxide ion vacancies.

Hydrogen can also be introduced electrochemically. Electrochemically-driven ion exchange occurs in a number of electrode reactants in lithium systems, where it is sometimes called "extrusion". There are also many mixed-conducting electrodes in which ions and their charge-compensating electrons are simultaneously introduced.

The principles involved in these various cases will be discussed.

The presence of hydrogen and/or water in oxides can cause significant changes in their reaction with lithium. Experiments have been undertaken to investigate the reaction of lithium with several materials, both with and without the initial presence of hydrogen or water within their structures. The significant changes that have been observed in the variation of the potential with lithium content in these various cases will be reported.

[1] S. Stotz and C. Wagner, Ber. Bunsenges. physik. Chem. 70, 781 (1966)