

FAILURE OF CATION AND ANION-CONDUCTING MATERIALS IN ELECTROCHEMICAL DEVICES UNDER INTERNALLY GENERATED PRESSURE

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Several electrochemical devices such as batteries, fuel cells, electrolyzers are either currently under development and/or are routinely used in many commercial applications. Highly publicized applications involve automotive transport, stationary energy storage, consumer electronics, etc. Recent incidences of the failure of Li-ion batteries in Boeing 787 plane, or Tesla's electric vehicle, are vivid reminders that batteries can catastrophically fail. Another example of the failure of batteries is the unexplained explosion of NGK's several MWh Na-S battery installation in Japan in September 2011. In the case of both the Li-ion battery and the Na-S battery, the formation of crack-like metallic dendrites is known to be one of the modes of battery failure [1]. Fuel cells and solid electrolyte based electrolyzers are at the present not commercial products but are being deployed as prototype units. These devices are also known to degrade or fail under various operating conditions, albeit in a much benign manner. For example, it is known that electrode delamination is one of the principal modes of failure [2]. Thus, in both types of devices, failure involves the formation of cracks under electrochemical conditions. Both types of failures can be explained by the formation of 'internal cracks' although there are differences in the nature of failures. In batteries based on metallic cation conductors (lithium ion or sodium ion), metallic dendrites form which can run across the width of electrolyte thus causing shorts. By contrast, in fuel cells and electrolyzers based on anion conductors (or proton conductors), failure manifests as electrode delamination. Thus, in the former case, cracks form along the direction of electrical current. In the latter case, by contrast, cracks occur perpendicular to the direction of current. Figure 1 compares fluxes to internal cracks in anion conductors and in metallic cation conductors.

The objective of this presentation is to analyse a coupled electrical-mechanical problem that describes the formation of cracks in metallic cation and anion conductors and their extension under electrochemical conditions. The formation and the extension of cracks under electrochemical conditions differs from failure under externally applied loads in one important respect. When subjected to external loads, the entire body is under stress. When the failure criterion is met at the tips of one or more cracks, unstable crack growth can occur depending upon the geometry. In such a case, driving force for crack extension is derived from the stored strain energy in the body at remote locations from the crack (e.g., failure under fixed grips or fixed load). Under electrochemical conditions, pressurization can occur

directly on crack surfaces (internal) and there is no external load applied. In such a case, there is negligible strain energy stored at remote locations from the crack. Thus, there is no driving force for catastrophic crack growth. Failure under internally generated pressures thus must occur in a stable manner; more material must be deposited inside a crack to exert pressure and extend the crack. The criterion for the occurrence of stable crack growth in anion conductors is given by

$$\frac{dK_I}{dc} = -\frac{2p}{\sqrt{\pi c}}$$

where K_I is the mode I stress intensity factor, p is the pressure on the crack surface, and c is the crack radius. The equation shows that as the crack extends at fixed total amount of deposited material in the crack, the stress intensity factor decreases. This means more material must be brought into the crack – leading to stable crack growth. Crack extension thus occurs in a stable manner, the rate of which depends nominally upon the electrical current flowing through the material. Theoretical results on the modelling of crack growth in two types of ionic conductors will be described. The theoretical results will be further extended to identify conditions under which propensity for the failure of the corresponding electrochemical devices (fuel cells, electrolyzers, batteries) can be minimized thus ensuring safe and stable operation.

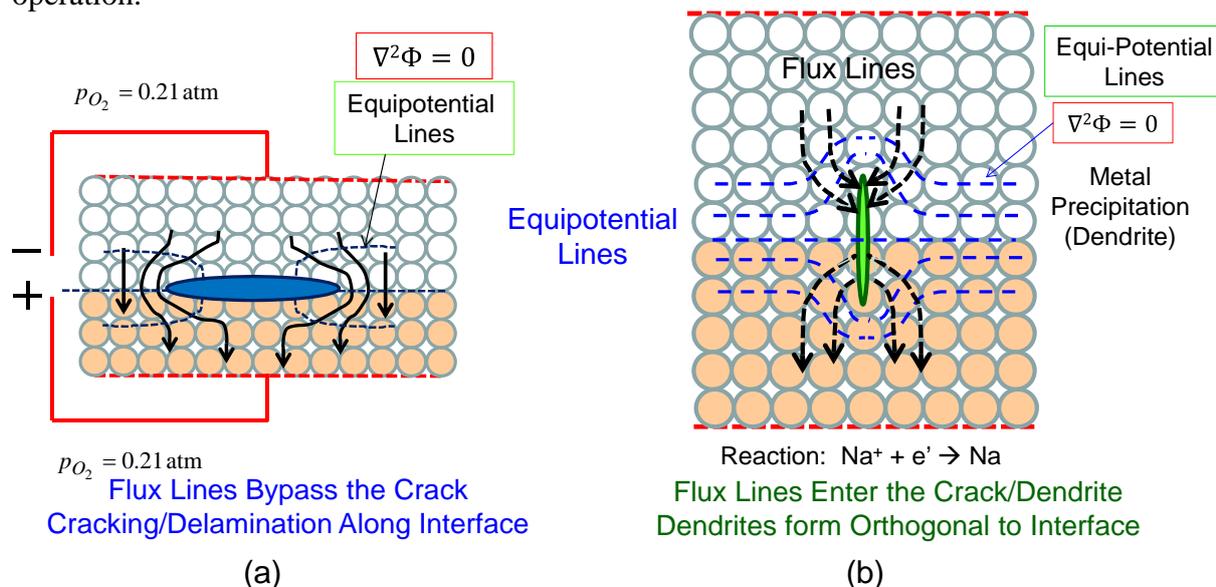


Figure 1: (a) A delamination crack in an anion conductor (e.g. O^{2-} ion conductor). The crack forms perpendicular to the direction of current. (b) A metallic dendrite in a metallic cation conductor (e.g. Li^+ or Na^+ ion conductor). A dendrite forms parallel to the direction of current.

REFERENCES

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