Hidden in Plain Sight: Understanding and Exploiting Systematic Couples to Improve Batteries

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Endeavors in electrochemical energy storage are industrial masochism for the same reason they are academic hedonism: a working, rechargeable battery represents a tight coupling of multiphase phenomena across chemical, electrical, thermal and mechanical domains. Despite these couplings, most treatments of batteries in the academic literature emphasize the material challenges and opportunities as opposed to the system level workings. There are at least three good reasons for this: 1) to date, tools for examining the structure of "real" cells in operando are largely limited to synchrotron x-ray and neutron methods, 2) full cells are products engineered for application demands and not platonic ideals and 3) material improvements can have enormous impact on battery performance.

Yet understanding and examining the physical dynamics of cells in a "scaled context" is still a worthwhile academic endeavor. The battery as a system presents problems that are difficult to decouple, but the study of such problems can introduce new opportunities and inform electrochemical reactor designs and material utilization strategies. In this review of systematic couplings of batteries we will discuss relationships that are "hidden in plain site" that can lead to new understanding of electrochemical behaviors and improved performance of batteries. Through this approach, and by studying full "scaled" cell behaviors we have learned how to compensate for certain material disadvantages and to create batteries and components that can meet performance targets which challenge traditional materials-first strategies.

First I will discuss physical couplings beyond the Ragone plot. For example, the relationship between energy density and power density is well described by the Newman Macro-homogenous model, but hidden in the implicit goal of the Ragone plot ("up, and to the right") is the lurking spectre of safety. An electrochemical cell with an energy density greater than 500 Wh/l and power density of 5,000 W/l can release all of its energy in at least 6 minutes, and in a poorly controlled environment the heat release can be a significant issue. I will examine the ramifications of this extra coupling, which makes a triplet between energy density, power density, and safety, and then apply cost constraints to show that when all the couples are put together an "unfortunate tetrahedron emerges."

Then, by examining the operating parameters for battery, I will show that the "dendrite" may not be the universal anathema it is made out to be (at least in a water stable system). Conventional wisdom conflates "flat" metal structures with equilibrium behavior, and equilibrium behavior with predictable. This conventional wisdom persists despite the 100 years of experimental evidence that near equilibrium cycling is difficult to predict for plate metals. We looked to see what happens when zinc is formed well beyond the limiting current and found that the zinc takes on a "hyper-dendritic" morphology that is seldom reported in the literature, and never used within a battery. This zinc grows in a manner that is at first glance counterintuitive: a nearly superconformal foam. TEM analysis indicates that true diffusion limited growth is taking place, but at the nanoscale. At the micron scale, what is observed is a collection of anisotropic dendrites growing in a controlled fashion as a “foam front”. Most interesting is that this foam has a different electrochemical potential than “bulk zinc” (50 mV less reducing than bulk zinc), likely because the active surface is edge-dominated as opposed to face-dominated. When we repeatedly charge and discharge this “hyper-dendritic” form of zinc to 50% of its capacity, the foam becomes progressively more compact, growing “inwards”, instead of forming the usual large anisotropic protrusions. This performance compares favorably with zinc foams produced through other methods. We believe this happens because every growth site is equally favorable (or unfavorable). In other words, when we form the zinc far from equilibrium conditions (high rate, well beyond the limiting current), and cycle the zinc close to equilibrium conditions (low rate, well under the limiting current), the zinc “cycles toward flat.” This is in contrast to the prevailing wisdom that plate metal batteries need to be flat. In further studies we are confirming that the highly-dendritic zinc formed in this manner cycles in a more predictable fashion than “bulk” zinc, and the even reaction rate across the surface of the foam retards ZnO passivation significantly.

Finally, in recent years the link between mechanics and batteries has become clear, but in most studies mechanics have followed chemistry: if the chemical degradation mechanisms is understood, then a mechanical investigation can be designed, but there has not been a “theory of mechanics” which could be applied to all batteries.

Driven by our systematic studies, my group saw that in any closed battery, mass cannot enter or leave the system, but mass must move within the battery. If the mass redistributes in a fixed volume, than the density must redistribute as well. This hints that sound might be the key for understanding batteries, inherently, as mechanical, and providing a tool which leads the chemistry. My group explored the correlation between state of charge, state of health, cycle number and acoustic interrogation using off the shelf non destructive ultrasonic testing equipment designed for large structural analysis (e.g. bridges and buildings). We found the correlation to be strong for both lithium ion and zinc alkaline batteries. I then superimposed two simulations of a battery, an electrochemical simulation and a dynamic pressure simulation using to track the acoustic behavior based on the density distribution dictated by the electrochemical model: the trend matched the experimental results quite well. The physics fell into place: any closed battery, regardless of chemistry, is a reactor in which density must redistribute as a function of state of charge. In most batteries, as the elastic modulus of electrodes change as a function of state of charge as well, it then follows that the sound speed is a function of charge and state of health.