Tailoring the Ragone Plot Through Microstructural Design of Battery Electrodes

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We have investigated whether the widely-recognized tradeoff between power density and energy density in battery systems can be ameliorated by controlling the internal structure of battery electrodes. Batteries of layered or laminated construction are typically constructed with microstructurally uniform electrodes. For example, particulate-based anodes and cathodes used in rechargeable lithium batteries usually have uniformly distributed porosity and particle size (except for unintentional gradients due to manufacturing processes). Previous models of lithium ion batteries [1,2] have likewise assumed uniform porosity through the thickness of the anode or cathode. However, since gradients in electrical potential and ion concentration arise within the electrodes as a natural consequence of charging and discharging, we infer that *intentionally graded electrodes* can have improved electrochemical performance compared to uniform ones.

Because a high packing fraction of the storage compound is generally desired to increase energy density, ion transport through the electrolyte-filled pore network is most often the rate-limiting transport step in a lithium ion battery. Spatially-varying porosity can therefore be used to optimize local ion transport for maximum electrode utilization and power density. We modified the model of Doyle, Fuller and Newman [1,2] to allow computation of charge-discharge characteristics for electrodes with a variety of porosity gradients [3]. Except for the porosity variations, the materials and systems parameters used in the model are typical of a lithium rechargeable battery.

Figure 1 illustrates results in the form of specific energy density vs. discharge current density curves for a battery containing a 100 μm thick MCMB carbon anode of uniform microstructure, and a 200 μm thick $LiMn_2O_4$ cathode with various linear porosity gradients (additional details of the model will be presented in the talk). The total pore fraction of the cathode was maintained at 0.3 throughout. In the legend, the two numbers give the pore fraction at the cathode-separator interface and the cathode-collector interface, respectively. It is seen that at very low current density, the curves converge since all cases have complete cathode utilization. At very high current density, they again converge at zero utilization. However, at intermediate current densities, the specific energy density varies dramatically with the sign and magnitude of the porosity gradient. At 15 A/m^2, an appropriately graded electrode can have nearly twice the energy density of a homogeneous electrode. The corresponding Ragone plot, Figure 2, shows the "knee" moving outwards for cathodes with higher porosity towards the separator side, where the ion current density is greatest during charge and discharge.

These results demonstrate a first-level of microstructure control through which significant increases in power density can be obtained without sacrificing energy density. In the talk, additional optimization schemes will be discussed. Results for lithium metal batteries, additional configurations such as parabolic gradients of positive and negative curvature, and still more radical microstructural modifications, will be presented. Fabrication schemes for batteries with engineered microstructures will be considered.

References

1. M. Doyle, T.F. Fuller and J. Newman, *J. Electrochem. Soc.*, **140**, 1526 (1993).
2. http://www.cchem.Berkeley.edu/~jsngrp/fortran.html
3. B. Hellweg, *Microstructural Modeling of Lithium Battery Electrodes*, S.M. Thesis, MIT, 2000.

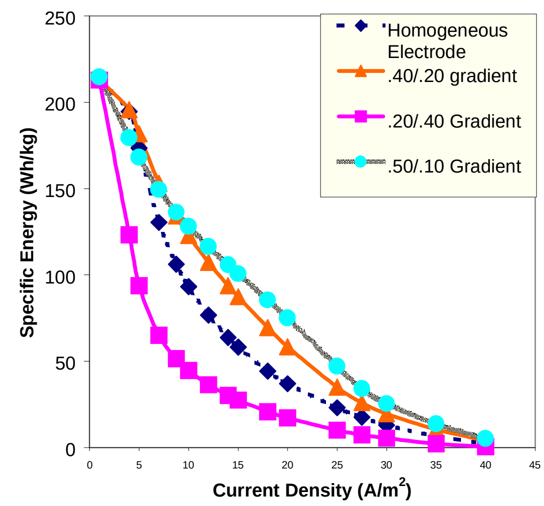

Figure 1. Computed specific energy density vs. current density for lithium ion batteries with cathodes of homogeneous and linearly varying porosity.

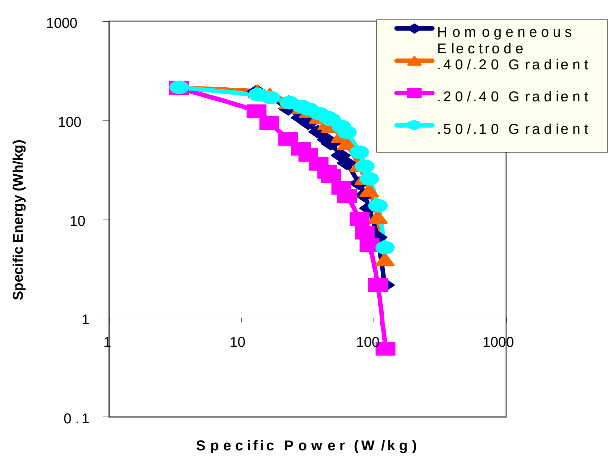

Figure 2. Ragone plot for batteries in Fig. 1.