Introduction to the Materials Science of

Rechargeable Batteries

Week 5: Battery Architectures and Design Guidelines
Lecture 5.3: Advanced Battery Architectures

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Classic Design Drawbacks

- Hard to control random events
- Will always have to traverse the entire cathode+separator+anode, especially in the limit of thick electrodes
- Total energy will always be diluted in an attempt to access higher power densities
- It is bulky!
Porosity Engineering

\[ \varepsilon = \varepsilon_0 + a \left( \frac{x_r}{h_c} \right) + b \left( \frac{x_r}{h_c} \right)^2 + c \left( \frac{x_r}{h_c} \right)^3 + \ldots \]
\[ \varepsilon(x) = 0.4 - 0.3 \left( \frac{x}{h_c} \right)^2 \]

\[ \varepsilon(x) = 0.25 + 0.15 \left( \frac{x}{h_c} \right)^2 \]
Ultra High Energy Density Designs

Figure 2. A) An exploded schematic view of the microbattery components. The cathode is attached inside a gold “can” using conductive carbon, while the lithium foil anode is attached to the copper lid. A film of insulating Li–P–O–N glass is deposited onto the can flanges. An intervening microporous separator is placed between the flange and the lid. The two halves of the cell are sealed using a fast-setting, photocured adhesive. B) Schematic view of parallel assembly of multiple batteries enabled by the fabrication process. C) Photograph of electroformed gold 64 can array. D) Packaged microbattery compared to US penny.
Processing High Diffusion Paths

Figure 2. Outline of the electrode fabrication process. Co-extrusion produces macro-pore channels, with controlled channel spacings. Lower row shows optical images of the green body before binder burn-out and sintering for different sample generations. Gen 0, Gen 1, Gen 2, and Gen 3 correspond, respectively, to the initial feed rod and the assembled structures after the 1st, 2nd, and 3rd extrusion passes. The darker dots (visible to the eye in Gens 0–2) are composed of carbon black and polymeric binder and leave aligned macro-pore channels after burn-out.

Figure 3. Gen 3 sample microstructure, generated by three co-extrusion iterations followed by binder burn-out and sintering. A) Low- and B) high-magnification SEM images showing polished top surfaces. C) Low- and D) high-magnification SEM images of sample in cross-section. This electrode has aligned channels ~6 micrometers in diameter, with an average channel spacing of 17 micrometers.

3D Battery Architectures
only an advantage if \[
\frac{h_s}{l} > \frac{\kappa_s}{\kappa_c}
\]
More 3D Battery Architectures
Ohmic Limited 3D Electrodes

\[ x_r = r \pm \sqrt{r^2 - \frac{2irt}{q}} \]

\[ \phi = U - \left( \frac{h_s}{\kappa_s} + \frac{r^2}{2h_c\kappa_c} + \frac{h_c}{\kappa_c} \right) i - \frac{r \pm \sqrt{r^2 - \frac{2irt}{q}}}{\kappa_c} i \]

\[ \frac{\kappa_s}{\kappa_c} \ll \frac{2h_s h_c}{r^2 + 2h_c^2} \implies \text{need VERY skinny columns} \]
Self-Organizing Batteries
More Self-Organizing Batteries

- Material 1: cathode storage compound
- Material 2: electrolyte/binder
- Material 3: anode storage compound

Percolative Network of Material 1
Bipolar Electrochemical Junction
Percolative Network of Material 3
Electron flow
Load/source
Self-assembled polystyrene particles

Glass

Electrodeposited nickel scaffold

Gold/chromium

Etch polystyrene

Electrodeposited NiSn anode material

Electrodeposited MnO₂ cathode material

3D cathode (LiMnO₂ on porous Ni)

3D anode (NiSn on porous Ni)

NiSn on porous Ni

LiMnO₂ on porous Ni

Anode Cathode Anode Cathode

J.H. Pikul, H.G. Zhang, J. Cho, P.V. Braun, and W.P. King “High-power lithium ion microbatteries from interdigitated three-dimensional bicontinuous nanoporous electrodes.” NATURE COMMUNICATIONS | 4:1732 | DOI: 10.1038/ncomms2747
Figure 3 | Ragone plot showing the performance of our microbattery cells and conventional power technologies. The energy and power density of our microbattery cells (A–H) at low to high C rates, along with previous microbattery cells having 3D electrodes (MB1 through MB3). The plot also includes the performance range of conventional power technologies and commercial batteries from A123 (high power) and Sony (high energy).

Figure 2 | Electrochemical properties of the microbattery. (a) Discharge from microbattery cell H at C rates ranging 0.5–1,000. (b) Capacity of microbattery cell H for the first 15 cycles at the noted C rate, normalized to the energy at 0.5 C. The secondary y axis indicates the percentage of capacity retained in the given cycle when compared with the previous cycle (calculated for low C rate cycles only).
Semi-Solid Flow Battery

Figure 2. a) Viscosity versus shear rate for suspensions of nanoparticulate carbon (Ketjen black) and LiCoO$_2$ (LCO) in alkyl carbonate electrolyte. The suspensions show shear-thinning behavior consistent with the presence of Ketjen networks partially disrupted by shear stress. b) Nyquist plots for the different suspensions and their components. The high frequency intercept on the real axis provides the ionic conductivity, and is the same for the pure alkyl carbonate electrolyte and the 0.6% Ketjen suspension in the same electrolyte (Z = 55 Ω intercept corresponds to 22 mS cm$^{-1}$ ionic conductivity since cell configuration factor = 1.2 cm$^{-2}$). At higher solids fractions the ionic conductivity decreases, e.g., the slurry containing 22.4% LCO and 0.6% Ketjen has 6 mS cm$^{-1}$ ionic conductivity (Z = 200 Ω). The 22.4% Li$_4$Ti$_5$O$_{12}$ (LTO) + 0.6% Ketjen suspension uses dioxolane solvent (1 M LiPF$_6$) and has lower ionic conductivity of 1 mS cm$^{-1}$ (Z = 750 Ω). The electronic conductivity, extrapolated from low frequency data, is about 10$^2$ lower than the ionic conductivity, being 0.06 and 0.01 mS cm$^{-1}$, for the LCO + Ketjen and LTO + Ketjen suspensions, respectively. c) Wet-cell SEM images of Ketjen black in alkyl carbonate electrolyte show extended percolating networks formed by diffusion-limited cluster aggregation, whereas in (d) a suspension of 22.4 vol% LCO and 0.6 vol% Ketjen in the same electrolyte shows uniform distribution of LCO particles. e) A 3D reconstruction of a 10 vol% LCO and 0.6 vol% Ketjen suspension obtained using X-ray tomography shows clusters of LCO particles without apparent long-range percolation.

Figure 3. Semi-solid half-flow-cell test: multistep galvanostatic charge/discharge of LiCoO$_2$ suspension (22.4 vol% solids (11.5 m), 0.7 vol% Ketjen, 1.3 m LiPF$_6$ in a blend of alkyl carbonates) flowing at 20.3 mL min$^{-1}$, separated from stationary Li metal negative electrode by microporous separator film.

Figure 4. Intermittent-flow SSFC tests: a) five iterations of semi-solid injection followed by constant-current constant-voltage charging for a half-flow-cell using LiCoO$_2$ suspension (10 vol% with 1.5 vol% Ketjen black, 1.3 m LiPF$_6$ in alkyl carbonate blend). b) Two iterations of injection and galvanostatic cycling for a full lithium-ion flow cell operating between 0.5 and 2.6 V at C/8 rate. Suspensions are 20 vol% LiCoO$_2$, 1.5 vol% Ketjen black and 10 vol% Li$_4$Ti$_5$O$_{12}$, 2 vol% Ketjen black, both in 1 m LiPF$_6$ in dimethyl carbonate.