Simulation of Electrolyte Composition Effects on High Energy Lithium-Ion Cells

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An important feature of the DUALFOIL model for simulation of lithium-ion cells [1,2] is rigorous accounting for non-ideal electrolyte properties. Unfortunately, data are available on only a few electrolytes [3,4]. However, K. Gering has developed a model for estimation of electrolyte properties [5] and recently generated complete property sets (density, conductivity, activity coefficient, diffusivity, transport number) as a function of temperature and salt concentration. Here we use these properties in an enhanced version of the DUALFOIL model called DISTNP, available in Battery Design Studio [6], to examine the effect of different electrolytes on cell performance. Specifically, the behavior of a high energy $LiCoO_2$/graphite 18650-size cell is simulated. The ability of Battery Design Studio to simulate 18650-size cells has recently been discussed [7].

Typically 18650-size cells are used in consumer electronics, most notably laptop computers, where they are expected to operate at ≤ 2 C rates and temperatures down to -10°C.

Properties of the following electrolyte sets were computed by K. Gering:

1) Equal concentrations of LiPF6 and LiDFOB in EC:PC:DMC
2) LiFSI in EC:EMC
3) LiPF6 in EC:EMC
4) LiFSI in EC:EMC:GBL
5) LiFSI in EMC:DEC
6) LiPF6 in EC:PC:DMC
7) LiPF6 in EC:DEC:DMC:EP
8) Equal concentrations of LiPF6 and LiFSI in EC:DMC:EMC
9) LiPF6 in EC:EMC:DMC
10) LiPF6 in EC:EMC:DEC
11) LiTFSI in PC:DME
12) LiCF3SO3 in PC:DME

Typically electrolyte property values were available in 10 °C increments from -30 to +60 °C. The values at each temperature were fit to Bezier curves, and then linearly interpolated to estimate values at intermediate temperatures. The virtual cell used for testing consisted of a LiCoO2/graphite chemistry with 2.4 Ah capacity weighing 47 grams and an active area of 0.0639 m^2.

As a first step the effect of salt concentration on the electrolyte LiFSI in EC:EMC (3:7 by weight) as examined (Figure 1) on C/2 discharge rates at -20 °C; simulations at +20 °C showed no effect of salt concentration and delivered ~3.6 Wh. The low capacity at -20°C is attributable to transport limitations; the salt in the positive electrode became depleted during the discharge. For examination of other electrolyte systems, a concentration of 1 molar was selected.

The discharge voltage profiles for a1.2 A discharge at +20°C of cells for each of the dozen electrolytes listed above were obtained by simulation and presented in Figure 2. The composition of the electrolyte had almost no effect on discharge energy at the C/2 rate.

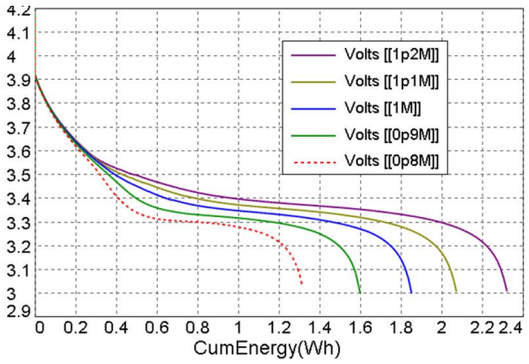

Figure 1 Simulated discharge curves at -20°C and 1.2 A with LiFSI in EC:EMC (3:7 by wt.).

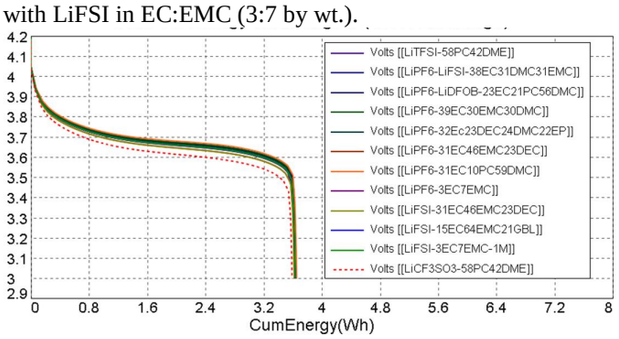

Figure 2 Simulated discharge curves for at +20°C and 1.2 A.

At lower temperatures, the discharge energy depended dramatically on the specific electrolyte system. The behaviors are explained based on the properties of the electrolytes and challenges to this simulation work are discussed.

References

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