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Thermochemistry and Equilibration Time Scales for a Rechargeable Lithium Ion Battery

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ABSTRACT

The open terminal voltage of a lithium ion battery is measured at temperatures ranging from 0 °C to 50 °C in increments of 10 °C. Primary focus is on three states of charge of the battery (full charge, late life, charge depletion). Estimates of the enthalpy, ΔH, and the entropy, ΔS, of the battery reaction are made using the established thermochemical relationship between the open terminal voltage and the Gibbs free energy, ΔG. As expected, ΔS is found to be dependent on the state of charge. The enthalpy also shows some dependence on the state of charge, which is at variance with the ideal Nernstian behavior. This may attributed to non-equivalence of intercalation sites as well as near neighbor interactions. Furthermore, the rate of discharge has little apparent effect on these results. An equilibration time well in excess of 20 hours is also observed.

1. Introduction

With the move toward renewable energy, power management and energy storage has gained increased attention [1–3]. Incorporating a network of ultracapacitors into the power system is an established method of improving battery performance and charge life [4–14]. Furthermore, effective power management also retards degradation resulting from multiple charge/discharge cycles [15]. Coupling of the capacitor bank can be achieved passively (e.g. hardwiring the capacitors in parallel with the battery), or actively (e.g. through a switch managed by a feedback loop). More detail on these control schemes is given elsewhere [16].

Active power management systems require monitoring the state of charge and health with metrics such as coulomb count and internal resistance. The motivation of this study was to evaluate use of the open terminal voltage (OTV) as one of the battery metrics. Such use requires a precise definition of the relationship between the OTV and the state of charge (SOC). The ideal Nernst relationship may be used as a starting point, and may be derived by assuming Langmuir-like coverage of the intercalation sites.

$$\varepsilon = \varepsilon^0(T) - \frac{RT}{F}\ln\frac{\theta_{cat}(1-\theta_{an})m_{an}}{(1-\theta_{cat})\theta_{an}m_{cat}} - (t_+ - t_-)\frac{RT}{F}\ln\frac{m_{cat}}{m_{an}}$$

Where ε is the electrochemical potential (numerically equal to the OTV), R is the ideal gas constant, F is the Faraday constant, T is the absolute temperature, t_+ and $t-$ are the transference numbers of the cation and anion, m_x is the formal concentration (more precisely, the activity) of the cation at the anode and cathode and θ_x is the fractional occupation of the intercalation sites at the anode and cathode.

The first term, ε^0, depends only on the temperature. In this context, ε^0 is not the "standard cell potential" unless the temperature happens to be 298 °K. The second term is the usual Nernst correction for concentration (more precisely, the activity) of the reacting species. The last term is the "junction potential", and arises because of charge transfer across the boundary between the anode and cathode. Both the Nernstian correction and the junction potential are linearly dependent on temperature. In electrochemical analyses, the junction potential is a nuisance, because it is a complicating factor that contributes nothing to the electrode reactions. Therefore, the medium is usually chosen such that the transference numbers are nearly equal, (e.g. aqueous KCl is a favorite of electrochemists; $t_+ - t_-$ for aqueous KCl is −0.02). However, in the case of a lithium ion battery, it may be beneficial to

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have the current carried only by the cations, $t_+ = 1$ and $t_- = 0$. In this case the effect of the lithium ion concentrations from the Nernst correction and the junction potential cancel exactly, leaving only the correction from occupation of the intercalation sites.

$$\varepsilon = \varepsilon^0(T) - \frac{RT}{F}\ln\frac{\theta_{cat}(1-\theta_{an})}{(1-\theta_{cat})\theta_{an}}$$

Such a situation is realized if the counter ion is highly immobile, in a gel polymer for example, or in the extreme, the polymer portion of a cation exchange resin. Until recently such resin systems, while allowing high transference numbers for the lithium ion, have not provided sufficient ionic conductivity to be of practical use [17]. A theoretical discharge curve for a lithium ion battery may be obtained by using a value of 3.75 V for ε°, and assuming $SOC = \theta_{an} = 1 - \theta_{cat}$. (This need not be the case for an actual battery, but it serves for the discussion here.) This curve is shown in Fig. 1, and reflects the known behavior for battery discharge; initial rapid drop in the OTV from a high voltage to the nominal operating voltage of the battery, followed by a slow drift downward until depletion, after which the OTV rapidly drops.Thermodynamic quantities may be calculated from the temperature dependence of the OTV, as follows from the identity, $\Delta G = -nEF$, where n is the number of electrons involved in the cell reactions, here n=1.

$$\Delta S = F\frac{\partial\varepsilon}{\partial T} \qquad \Delta H = -F\frac{\partial(\varepsilon/T)}{\partial(1/T)}$$

Substitution of the indicated differentials yields the following equations for the enthalpy and entropy of the cell reactions.

$$\Delta S = F\frac{\partial\varepsilon^0}{\partial T} - R\ln\frac{\theta_{cat}(1-\theta_{an})}{(1-\theta_{cat})\theta_{an}} \qquad \Delta H = -F\frac{\partial\left(\varepsilon^0/T\right)}{\partial(1/T)}$$

Both entropy and enthalpy have a term related to ε° which is not dependent on the occupation of intercalation sites. Contributions from the adsorption energy (both electronic and vibrational) appear in the ε° term. However, the entropy has an additional occupation dependent term. The main point here is that the entropy has a functional dependence on the occupation of the intercalation sites, and the enthalpy does not; ΔS depends on the SOC, while ΔH does not, at least in the ideal case. Because the thermochemistry of lithium ion batteries has been reported elsewhere [18–23], the focus of this study was not on the thermodynamic quantities as an end in itself, rather as a practical way to evaluate use of the OTV as an input for active power management.

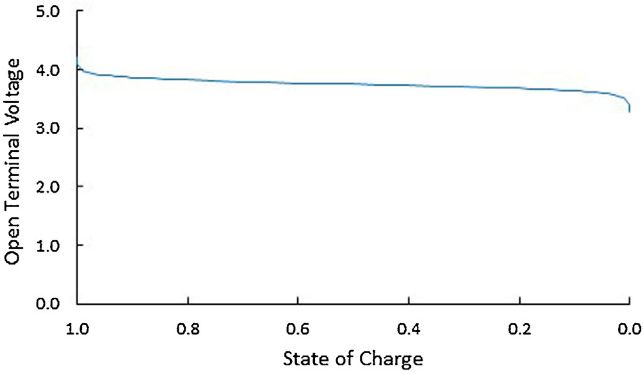

Fig. 1. Nesrnstian description of the OTV as a function of the relative SOC.

2. Experimental

A rechargeable, 3.6 V 1000 mA h Ultrafire LC 16340 lithium ion battery was used as the test specimen. Charging was accomplished by using the manufacturer's supplied charging pack. The battery was discharged to a predetermined level with a Hewlett Packard 6063 A electronic load. Three states were considered in each experiment (1) full charge, (2) after delivery of 1000 Coulombs, and (3) after delivery of 1320 Coulombs. Coulombs were "counted" by multiplying the set current of the electronic load by the time of discharge. After the battery was set to the desired state, it was placed in a Thermotron S-1.2 thermal cycle chamber, where the temperature was ramped from 0 °C to 50 °C in increments of 10 °C. Because the thermal equilibration time was not known the outset, the chamber was held at each temperature for three hours before ramping to the next set point. Thus the complete ramp was done over a period of 18 hours. Temperature and OTV data were logged with an Agilent 94970A data acquisition system. Data scans were done every 5 minutes.The first experiment was a simple discharge of the battery. The electronic load was allowed to draw 4 A for 5 seconds, after which the battery allowed to recover without load for 5 seconds. This was repeated to depletion of charge. In this one experiment, the voltage was logged at 1 second intervals. The battery was recharged using the manufacturer's recharger.

The next experiment was run in order to evaluate ΔH and ΔS at the three stages of discharge (fully charged, after 1000 Coulombs, and after 1320 Coulombs), when discharged at 0.5 A. These charge states were selected because they represent decision points in a power management system (when to stop charging, when the battery is nearing the end of its charge, and when the battery is near complete exhaustion). The fully charged battery was placed in the thermal cycle chamber for temperature ramping, as described above. During this time the temperature and OTV were logged at 5 minute intervals. Because the OTV was found to drift over the entire ramping period, the thermal ramp was repeated three times. Discharge was then performed with a current load of 0.5 A at the ambient laboratory temperature. After 33 minutes (1000 Coulombs), the battery was placed in the thermal cycle chamber for temperature ramping. Again, a persistent voltage drift was observed, hence the thermal was repeated three more times. The battery was then removed from the chamber and discharged for another 11 minutes at 0.5 A (additional 320 Coulombs passed) in the laboratory ambient. This was followed by a total of four thermal ramps.

After recharging the battery, ΔH and ΔS were again evaluated for the three charge states, this time with discharge being done at 0.2 A. Again, the electrical potential was found to drift throughout the first thermal ramp, so an additional three ramps were performed before continuing with the next evaluation. At the conclusion of this experiment, the battery was recharged at a slow rate, and the entire sequence repeated, except using a load of 2.0 A to discharge the battery.

The very long drift of the OTV raised a question as to whether or not charge rate would have an effect, the idea being that rapid charging does not allow lithium time to deposit evenly on the intercalation sites, but slow charging does. Therefore, a very slow charge rate was used to condition the battery for a discharge experiment conducted at 2.0 A. The battery, having been depleted of charge was recharged using a Tekronix P52520G programmable power supply, with current limiting capability. The voltage was set 4.2 V, and the current limit was set to 0.02 A, mild conditions which required overnight charging before the thermal ramping could be done. ΔH and ΔS were determined from the thermal ramping of the slowly charged battery.

In order to evaluate the voltage drift under isothermal conditions, the programmable power supply was used to charge