

The activation energy of self-discharge in anode and cathode for lithium-ion batteries

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Self-discharge is a common phenomenon in primary and secondary batteries. It results mainly from the thermodynamically predicted reactions between the electrolyte and the active electrode materials. As a matter of fact, most batteries in their charge state yield an open circuit voltage than can be wider than the stability window of the electrolyte. Therefore, the charge retention in a battery is mainly governed by the kinetics of the electrode/electrolyte reactions. The latter are usually thermally activated, which mean that the rate of self-discharge will increase with temperature.

Most studies on the self-discharge in lithium-ion batteries were conducted on a complete cell, usually based on the $\text{Li}_x\text{C}_6/\text{LiPF}_6$ organic carbonate/ Li_yCoO_2 chemistry. However, since both Li_xC_6 and Li_yCoO_2 are metastable versus the electrolyte, their kinetics of self-discharge may involve different mechanisms due to differences in their chemical potential. A separate study in half-cells will allow distinguishing between contributions each one of the electrodes to the total self-discharge and to the reversible and irreversible capacity losses.

1/The anode side: Li/1M LiPF_6 -EC(1):DMC(1)/graphite half-cells were cycled at ambient temperature under C/5 rate between 1.5 and 0V [1]. They were stored at different temperature between 55 and 80C for several days at the initial fully lithiated state LiC_6 . The open-circuit voltage (OCV) was monitored during the aging. The remaining capacity was determined during the first charge (de-lithiation) and the new reversible capacity was accessed by galvanostatic cycling at the ambient temperature.

The time dependence of the OCV was found according to the following phenomenological law:

$$E(T, t) = E^0(T) + \frac{RT}{F} \ln \frac{1}{(1 - x_\infty)e^{-kt} + x_\infty} + \chi(T, t) \quad (1)$$

Where $\chi(T, t) = \chi_o(T) + A(T)t + B(T)t^2 + \dots$ (2)

The time constant k was found to follow the Arrhenius law and the corresponding activation energy was determined to be $48.8 \text{ kJ} \cdot \text{Li-mole}^{-1}$. On the other hand, the total capacity loss was found to follow a first order kinetics law of the type:

$$Q(T, t) = Q_0 \exp(-\lambda(T).t) \quad (3)$$

where the time constant $\lambda(T)$ has an activation energy of $50.2 \text{ kJ} \cdot (\text{Li-mole})^{-1}$ close to the one of k in eqn. (1). This suggests that the capacity loss and the voltage change have similar mechanism, which we attributed to lithium reaction with the electrolyte, which ultimately transform to the solid-state interphase (SIE) that builds up on the graphite surface.

2/The cathode side: For practical reasons, we used 1M LiClO_4 electrolyte solutions in the Li/LiCoO₂ half-cells for the self-discharge study. Similar cycling was applied between 3 and 4.2 V at ambient temperature, and then cells in their charged state ($\text{Li}_{0.5}\text{CoO}_2$, 4.2 V initial) were maintained at constant temperature between 55C and 75C for up to 6 weeks [2]. Here the OCV curves followed different time dependence:

$$E(t, T) = E(0, T) - K(T)t^{1/2}, \quad (4)$$

$K(T)$ was found to obey the Arrhenius law with $41.3 \text{ kJ} \cdot (\text{Li-mole})^{-1}$ as activation energy.

The relative capacity total loss 'x' (in %) fitted with the following time equation:

$$t = ax^2 + bx + t_0, \quad (5)$$

where the 'a' constant was found to be thermally activated with $81.20 \text{ kJ} \cdot (\text{Li-mole})^{-1}$ as activation energy. The differences in the activation energy from the OCV and the capacity loss measurement suggest the corresponding kinetics governed by different mechanisms. As a matter of fact, the OCV related to the Li-diffusion from the electrolyte to the electrode bulk structure, while the capacity loss was governed by surface reactions and phase transformations.

This study highlights the usefulness of the half-cell configuration in the kinetics of self-discharge in lithium-ion batteries.

References:

- [1] Y. Reynier et al. IEEE 8576(2002)145
- [2] Y. Ozawa et al. Proc. 202nd Meet. Electrochem. Soc. Salt Lake City, Oct. 20-24, 2002, Abst. # 116

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