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Short Communication

Distinct view on batteries performance analysis

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ABSTRACT

Many mathematical models have been developed for Li-battery cells performances. However, a critical need still do exists for a rather simple battery performance evaluation method. In the present study, such a parameter, Integral average voltage (IAV), is being introduced. Its utility, convenience and applicability are validated via existing experimental data derived from Li-air batteries and lithiated Ni dope Mn spinel 5 V cathode materials. IAV is simple to calculate using the cell charge/discharge profile; at the same time, it offers a perceptive analysis of cell features and associated processes.

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1. Introduction

Li-related batteries are the most successful on the consumer electronic market; their usage is also gradually spreading to power sources for electric vehicles and energy storage for load levelling. Cost, safety, energy density and specific energy are the parameters, which are important for commercially viable and robust battery. Cell's discharge and charge voltages are both related to these parameters and thus, are among the most important cell characteristics. These parameters are important for practical battery applications [1] and are also particularly important in research and development (R&D) in the fields of battery chemistries and battery designs. In course of battery-related R&D works, cell's cathode and anode are usually being considered separately, assuming that $V_{cell} = V_a - V_c$ (V_a and V_c stands for anode and cathode potentials vs. a reference electrode, usually *vs.* Li^+/Li electrode).

Cell's over-voltage ΔV_{cell}, an additional important cell parameter, is defined as the difference between the electromotive force of the cell reaction V_{cell}^{emf} and the actual cell voltage V_{cell}. The value ΔV_{cell} indicates the related energy loss in course of charge transfer reactions as well as the internal battery *ohmic* resistance. When it comes to comparison of cells with the same chemistry but with different electrode design as well as different electrolytes, it is accepted that an advantageous design provides the smallest values of ΔV_{cell}. The value ΔV_{cell} depends on the anode over-voltage ΔV_a and cathode over-voltage ΔV_c, which are the differences between the actual electrode potential and the electromotive force of the anode V_a^{emf} and cathode V_c^{emf} reactions, respectively. The parameters V_{cell} and ΔV_{cell} depend generally on the charge being passed (Q), or the state of charge (SoC) [2,3] of the cell, Thus, all the above parameters are better to be denoted as $V_{cell}(Q)$, $\Delta V_{cell}(Q)$, $V_a(Q)$, $\Delta V_a(Q)$ and $V_c(Q)$, $\Delta V_c(Q)$. Fig. 1 illustrates for example, that these functions are diverse for different electrodes being utilized in Li-air battery design and therefore, a comparison of a particular battery design and chemistries in a selected SoC is rather quite difficult.

A possible solution for this problem is to compare electrodes and cells voltages at some (standardized) SoC; this approach resembles the industry-recommended method to measure cell's open circuit potential (OCP) after charge/discharge cycle at 4% of SoC [3]. The specific SoC value, which may be adopted, unavoidably is an arbitrary value. The example presented in Fig. 1 demonstrates that such approach may be quite confusing as SoC at a specific capacity of 0.5 Ah/g provides $\Delta V_c^{(I)} > \Delta V_c^{(II)}$ but SoC at 1 Ah/g is leading to inverse result as $\Delta V_c^{(I)} < \Delta V_c^{(II)}$.

2. Method of calculations

The obstacles described above may be overcome with the introduction of two new parameters: integral average cell (or electrode) *voltage*, $\overline{V_{cell}}$ and integral average cell (or electrode) *over-voltage*, $\overline{\Delta V_{cell}}$. These parameters can be implemented and applied both on discharging, as well as on charging processes evaluations. Specifically, the energy spent (or gained) in course of charge transfer through the potential difference $V_{cell}(Q_{final}) - V_{cell}(Q_{initial})$ is

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$$E = \int_{Q_{\text{initial}}}^{Q_{\text{final}}} V(Q)dQ \qquad (1)$$

Here, Q_{initial} stands for the charge of the cell at the beginning of the discharge (or charge) process, and Q_{final} stands for the charge of the cell at the end of the discharge (or charge) process.

Fig. 2 illustrates graphically Eq. (1), having the average integral voltage, over the $[Q_{\text{initial}}, Q_{\text{final}}]$ interval, being defined as:

$$\overline{V_{\text{cell}}} = \frac{\int_{Q_{\text{initial}}}^{Q_{\text{final}}} V(Q)dQ}{Q_{\text{final}} - Q_{\text{initial}}} = \frac{E}{\Delta Q} \qquad (2)$$

The average over-voltage over this interval may be defined as:

$$\overline{\overline{V_{\text{cell}}}} = \left| V_{\text{cell}}^{\text{emf}} - \overline{V_{\text{cell}}} \right| \qquad (3)$$

When one electrode (cathode or anode) is being considered, the exact calculations can be individually implemented with each electrode; integral average electrode voltages and integral average electrode over-voltages maybe denoted as $\overline{V}_a, \Delta\overline{V}_a$ and $\overline{V}_c, \Delta\overline{V}_c$ for the anode and cathode, respectively.

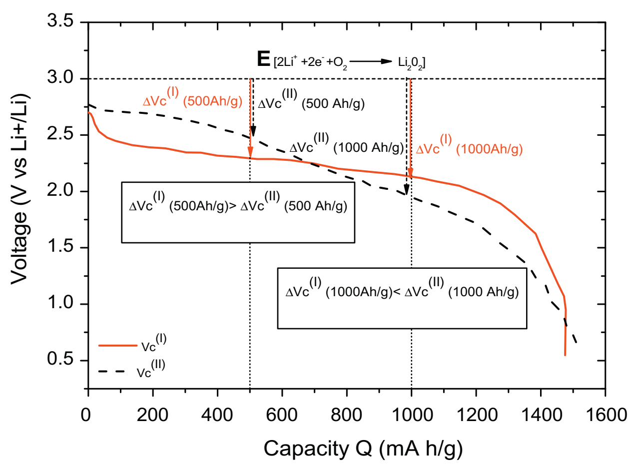

Fig. 1. Discharge profile curves of Li-air cathode – limited cells, air cathodes are made of different carbon materials; the cells operated in pure oxygen; curve (I) – solid red – is acquired from [4], i = 0.1 mA/cm^2, super-P carbon black cathode, curve (II) is acquired from [5], i = 0.2 mA/cm^2, meso-cellular carbon cathode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

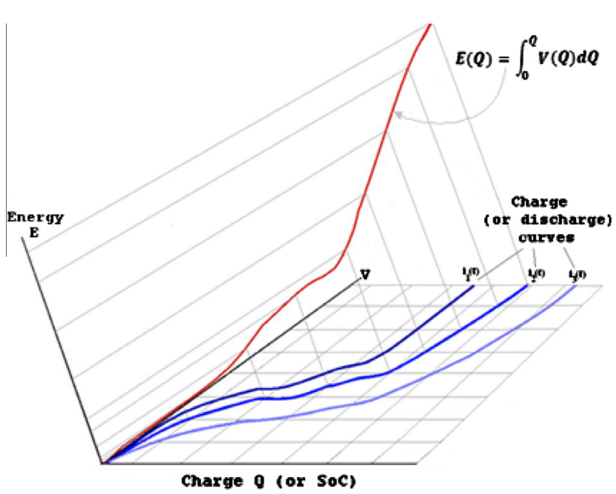

Fig. 2. Graphical representation of the cell (electrode) energy changes during charge (or discharge).

Routinely, the charge/discharge voltage and electrode over-voltage are of interest over the whole working interval. However, in a complete process, $Q_{\text{initial}} = 0$ and Q_{final} is the final cell capacity, Q_{full}; on this basis, the integral average voltage and integral average over-voltage being presented below, are calculated over $[Q_{\text{initial}}, Q_{\text{final}}]$ interval.

3. The applicability of the proposed concept

The examples provided in this paper are based on a well-known literature data on oxide cathode materials, having a spinel structure, demonstrate the validity, convenience and robustness of the approach. $LiMn_2O_4$ spinel attracted an attention as possible cathode materials candidates for Li-ion batteries because of its high energy density and low cost. Since pure $LiMn_2O_4$ demonstrates low cyclability, current research is focused on the single- and double-doped spinels $LiM_xMn_{2-x}O_4$ (M = Ni, Co, Cu, Cr, Fe, etc.), which have been reported to have operational voltages over 4 V, having an improved cycling performance, compared to pure $LiMn_2O_4$ [6–8]; the curves $V_{\text{cell}}(Q)$ for these oxides usually have a complicated shape and are inconvenient for comparison and further consideration, though.

A typical example of such research is the work of Singhal et al. [9], considering $LiMn_{2-x}Ni_xO_4$ spinels. The charge/discharge curves (shown in Fig. 3 [9]) demonstrate a strong dependence on Q, and in case of $x \neq 0$ the curves demonstrate two plateaus. Therefore, the curves are convenient only for qualitative consideration. The data presented in Fig. 3 were used for $\overline{V}_c$ calculations, and the results are presented in Table 1 and in Fig. 4.

The average integral voltages $\overline{V}_c$, as presented in Table 1, better assist identifying several correlations between different variables and thus, allow a better comprehensive analysis of the studied electrode system. For example, Table 1 reveals that $\overline{V}_c$ dependence on Ni content (x) correlates well with the dependence of Li partial intercalation energies on nickel content (Li partial intercalation energies resulted from ab initio quantum–mechanical calculations) [9]. It is remarkable that in course of cycling $\overline{V_{c(x)}}$ (charge) is practically unchanged, whereas $\overline{V_{c(x)}}$ (discharge) increases for $x > 0$. In order to discuss this feature; the following issues are to be considered.

First, Li^+ ion mobility has a major input on the cathode voltage [11]. Indeed, Li^+ ion migrates during charge within the Li-poor regions, from the oxide particle core toward the particle surface. Whereas, during discharge Li^+ ion migrates, vice versa, within the Li^+-rich regions, from the surface toward the grain interior; it

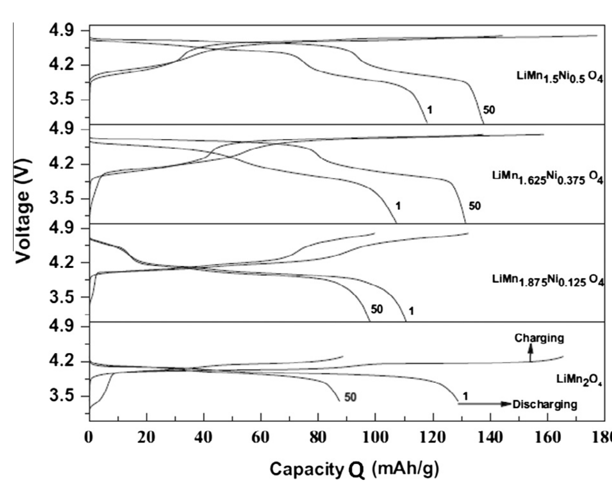

Fig. 3. Charge/discharge behaviour of $LiMn_{2-x}Ni_xO_4$ cycled in $LiPF_6$ + (EC + DMC)/Li coin cell (acquired from [9]).

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