

Lecture 14

Electrochemistry of the lithium-ion battery

Lithium-ion batteries (LIBs) are electrochemical energy converters that play an important part in everyday life, powering computers, tablets, cell phones, electric cars, electric bicycles, and numerous other devices. They can also be used to store intermittently produced renewable energy. The lithium-ion battery's immense utility derives from its favourable characteristics: rechargeability, high energy per mass or volume relative to other battery types, a long cycle life, moderate to good thermal stability, relatively low cost, and good power capability. These characteristics can be tuned to some extent using different transition-metal oxides or phosphates in the positive electrode. In recognition of the importance of lithium-ion batteries, the 2019 Nobel Prize in Chemistry was awarded to Goodenough, Whittingham, and Yoshino.

While most household lithium-ion batteries consist of a single electrochemical cell generating a cell voltage of around 3.4 V, batteries providing higher voltages can be constructed from several such electrochemical cells in series. A typical cell, see Figure 1, consists of two electrodes (negative and positive), a separator between the electrodes and an electrolyte that conducts ions but not electrons, as well as metallic current collectors on the electrodes that conduct electrons from the active materials to the external electrical circuit that allows the electrons to flow from the negative to the positive electrode.

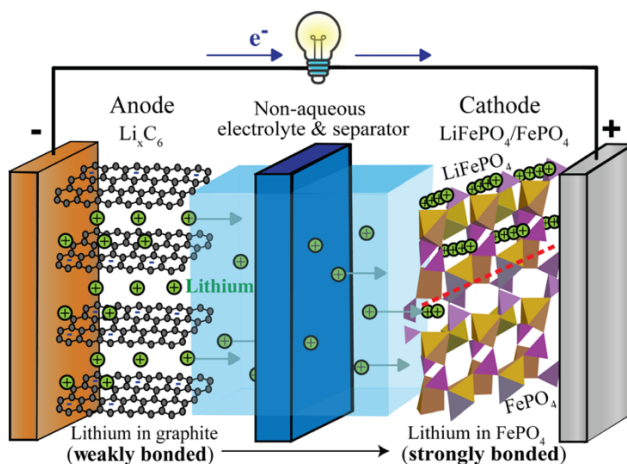


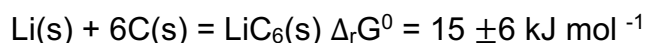
Figure 1. Schematic of a discharging lithium-ion battery with a lithiated-graphite negative electrode (anode) and an iron-phosphate positive electrode (cathode).

Figure 1 shows a schematic of a discharging lithium-ion battery with a negative electrode (anode) made of lithiated graphite and a positive electrode (cathode) of iron phosphate. As the battery discharges, graphite with loosely bound intercalated lithium ($\text{Li}_x\text{C}_6(\text{s})$) undergoes an oxidation half-reaction, resulting in the release of a lithium ion and an electron. The lithium ion crosses the electrolyte-soaked separator and moves to the $\text{FePO}_4(\text{s})$ cathode, where it enters and fills channels or tunnels in the iron phosphate, forming $\text{LiFePO}_4(\text{s})$.

Since the separator and electrolyte are electrical insulators, the electron must travel through the external circuit, giving off the energy released in the chemical reaction.

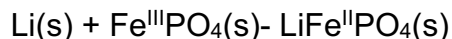
At the cathode, the electron is taken up by a transition-metal ion such as Fe^{3+} , Co^{4+} , or Mn^{4+} , or by oxygen. This process is energetically downhill because the weakly bonded lithium in Li_xC_6 is high in energy compared to more strongly bonded lithium in the positive electrode. Since lithium is bonded only relatively weakly to graphite sheets (see below), the lithiated graphite electrode stores a lot of chemical energy.

The **negative electrode** of a discharging lithium-ion battery is **the anode**. It consists of a conductive material where lithium is weakly bonded and easily released as a lithium ion while the electron is left behind in the electrode and passed on to the external circuit. In practice, lithiated graphite is the most widely used material for anodes. The intercalation of lithium from lithium metal into graphite can be written approximately as



The negative free energy change indicates that the intercalation is spontaneous: lithium is bonded slightly more strongly in graphite than in metallic lithium. Nevertheless, as demonstrated in the next section, the difference is small (<5%) compared to the difference in lithium bonding energy between the anode and the strongly ionically bonded cathode materials. This confirms that lithium is relatively weakly bonded in a graphite anode.

The electrical energy released per mole of lithium in the reaction of the widely used iron phosphate-based **cathode** materials



equals the free-energy change, $\Delta_r G^0 = -331 \text{ kJ mol}^{-1}$. The strongly negative values confirm that discharge in a lithium iron phosphate battery is energetically strongly downhill. According to the well-known relation

$$E_{\text{cell}} = -\Delta_r G^0 / F$$

with the Faraday constant $F = 96.5 \text{ kC mol}^{-1}$, the cell voltage is $E_{\text{cell}}^0 = 3.43 \text{ V}$.

The detailed nature of specific mechanisms, such as the effect of charge/discharge rate or prolonged cell cycling on the energy and power storage performance, is still not sufficiently understood. These aspects are crucial and strongly affect, e.g. the lifetime and cost of LIBs and must be implemented to improve the overall quality of a LIB device. In this regard, electrochemical impedance spectroscopy (EIS) could be considered as a useful technique that may generate insights to help solve the not yet addressed LIB issues.

Even when using symmetric or three-electrode cells, the number of elementary processes taking place in the cell may remain high and typically involves (i) transfer of electrons from the current collector to the electrode composite, (ii) electron conduction/migration across the composite electrode thickness, (iii) ion migration across the electrode thickness, (iv) electrochemical insertion of ion and electron into the active storage particles, (v) double-layer charging at solid/liquid interfaces, (vi) coupled diffusion of active and non-active ions in porous electrode composite, (vii) coupled diffusion of ion and electron inside the active storage particles and (viii) migration and diffusion of ions in separator. In fact, in the ideal case, EIS can detect separately more or less all of these processes as individual features in a single measured spectrum (Figure 2).

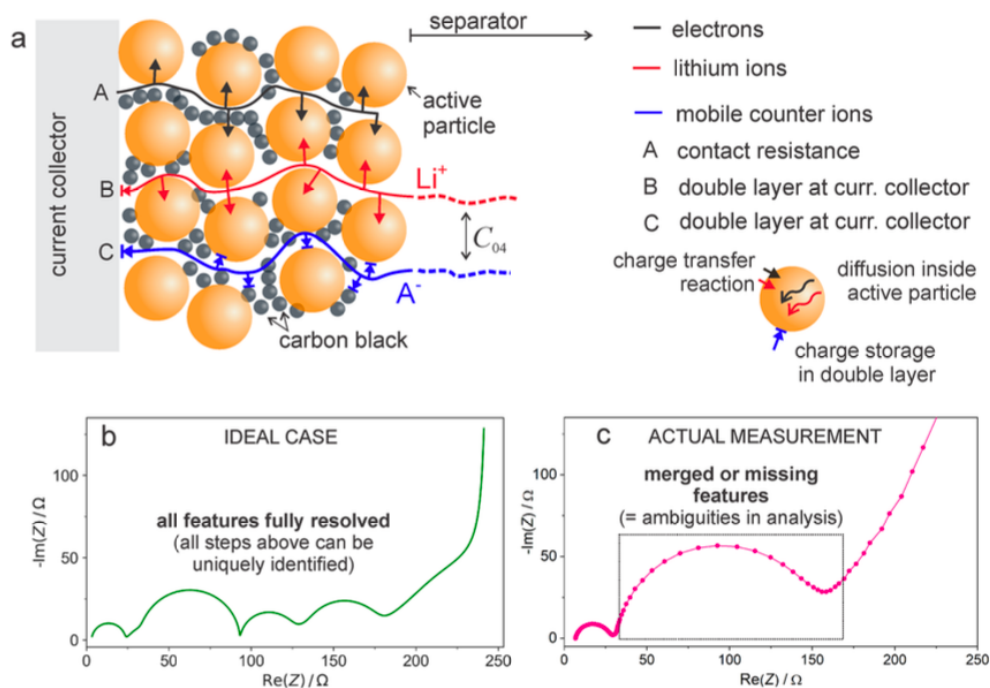


Figure 2. Typical processes in a lithium-ion battery electrode and their identification using electrochemical impedance spectroscopy measurements [1].

- Schematics showing the movement of electrons and mobile ions in a typical Li ion insertion positive electrode.
- Theoretical impedance response for an ideal case where each individual step shown in a can be seen as a separate feature.
- Example of a practical EIS measurement where many of the predicted features are not seen due to overlap of time constants, very small values of impedance values for certain steps or other measurement artefacts. Most of the missing features can be retrieved using dedicated electrochemical experiments, as explained in the main text.

To be precise: in the ideal case, the number of measured features is only one less than the number of individual processes which shows the capability of EIS to split the complex processes into their elementary steps. The problem is that many of these individual features overlap in realistic measurements, and it is rather challenging to decouple them unambiguously. This aspect is crucial and must be carefully considered to exploit EIS in the battery research field fully.

References

- Gaberšček, Miran. "Understanding Li-based battery materials via electrochemical impedance spectroscopy." *Nature Communications* 12.1 (2021): 6513.