

Performance of Li-ion batteries: contribution of electronic and ionic factors

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Different combinations of cathode and anode materials have been investigated for improving the energy content of Li-ion battery materials. One of the dominant factors of performance is related to the achieved battery voltage depending on the charging state of the battery. The voltage difference of the electrochemical cell is given by the change in the Gibbs energy for the exchange of Li which will again depend on the exchange of electrons and ions between the two phases. A systematic experimental study on the relative influence of both contributions on the measurable battery voltage have not been performed yet. Therefore we will present in this contributions surface science studies of well-defined thin film electrodes which allows to compare changes in electronic structure and related electronic surface potentials with voltage measurements. In addition, we will present first experiments on the direct measurements of the ionic work function.

A number of different thin film cathode materials with different composition of the layered oxides and olivine structural family have been prepared in recent years mostly by sputter deposition inside an integrated UHV system. Subsequently, the electronic structure and surface potentials as e. g. the electronic work function and the changes induced with charging have been determined by applying photoelectron spectroscopy. The experiments allow to relate energetic changes in the Fermi level positions to the measured battery voltage and thus deduce the relative contribution of the different electronic chemical potential to the battery voltage. Based on our data we conclude that the major contribution to the battery voltage is related to electronic work function variations of the different electrode materials.

In addition, we have performed first experiments by experimentally determining the electronic and ionic work function of a cathode material. Such experiments allow to directly determine the chemical potential of the Li atom as given by the electronic and ionic contribution in relation to the vacuum level. With a Born-Haber cycle we can show that the experimentally determined values are in reasonable correspondence to the battery voltage.

Summarizing our results we conclude that the performance of Li-ion batteries depend on the relative changes of bonding contributions for electrons and ions within the used electrodes with electrons providing the larger part to the battery voltage. Measured variations in performance must be related to deviations of the rigid band behavior of the electrode materials and to surface effects occurring in the given battery set-up.