

Electrode optimization and behavior of LTO/LFP electrodes for applications in lithium ion batteries

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Abstract

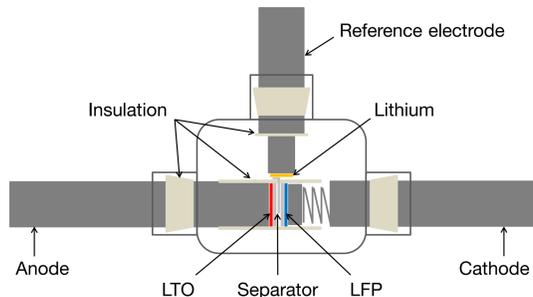
In order to reduce the consumption of fossil energies and to replace nuclear power plants, an appropriate storage system to store energy, from renewable sources like the wind and the sun, has to be developed. A battery system with a high cyclability, stable capacity and unhazardous substances is a suitable candidate. In 2010, Guerfi et al.^[1] demonstrated that a battery system consisting of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO) and lithium iron phosphate (LiFePO_4 ; LFP) shows a stable and constant discharge capacity for more than 20,000 deep cycles. Due to these results, the battery system LTO/LFP is a possible option for long term storage. This project is a cooperation of the Institute of Technical

Electrochemistry (Prof. Dr. Hubert A. Gasteiger) and the Institute for Electrical Energy Storage Technology (Prof. Dr.-Ing. Andreas Jossen). The financial support is given by the Munich based foundation Stiftung Nagelschneider.

The goal of this work is to investigate the detailed degradation mechanisms of the LTO/LFP system and to get a better understanding of the processes inside the electrode. Therefore, we focus on the impact of electrode composition and temperature on the cycle life. Further, we try to elucidate the degradation mechanisms in order to develop meaningful engineering models on aging and safety.

Electrode Preparation and Cell Design

Fig. 1 The cell design allows measurement of the electrode combination with reference electrode and a defined compressive force on the electrodes.



Electrode slurry contains active material (LFP or LTO), conductive carbon (SuperC65), a polymer binder (Kynar PVDF®) and N-Methyl-Pyrrolidone (NMP) as a solvent.

Mixture is coated on a current collector (aluminum or copper foil). Electrochemical measurements are cyclic voltammetry (CV), potentiostatic electrochemical impedance spectroscopy (PEIS) and galvanostatic cycling. Cells have a three electrode setup in a Swagelok® T-Fitting with a lithium foil as a reference electrode. In half-cells LTO or LFP is used as the working electrode and another lithium foil as the counter electrode. For full-cell measurements LTO is placed as the anode and LFP as the cathode (see Fig. 1). The electrolyte is 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). With the spring-setup it is possible to define a fixed pressure on the electrodes. This leads to a consistent and comparable quality of the tested cells.

Electrochemical Reactions

In Fig. 2 the charging process of a LTO/LFP cell is shown schematically. The charge begins with the oxidation of iron ions and the removal of lithium ions from the LFP crystal structure. The electrons travel towards the aluminum current collector and via an external circuit to the LTO side. With the reduction of Ti^{4+} to Ti^{3+} the lithium ions are stocked into the LTO structure. Due to a negligible variation of the cubic cell unit, this process generates no mechanical stress to the electrode which increases the cyclability. A relatively high insertion potential of lithium ions (1.55 V vs. Li/Li^+ [2]) avoids deposition of elementary lithium on the LTO anode and enhances the safety. The use of LFP as the cathode material minimizes electrolyte oxidation since the charging potential (3.50 V vs. Li/Li^+ [3]) is lower than the degradation potential of the used electrolyte.

The following reaction equations show the charging reactions on both anode and cathode:

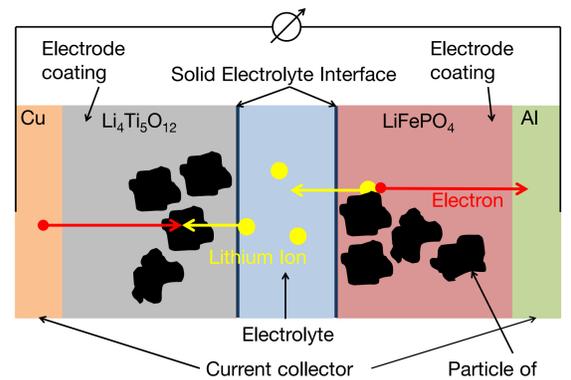
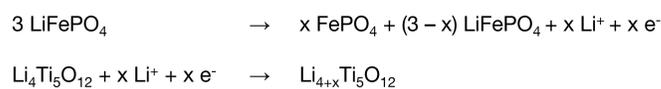


Fig. 2 Charging process of a LTO-LFP battery

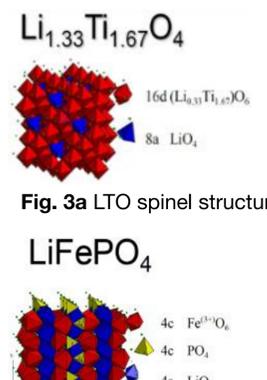


Fig. 3a LTO spinel structure

Fig. 3b LFP olivine structure

Measurements and Results

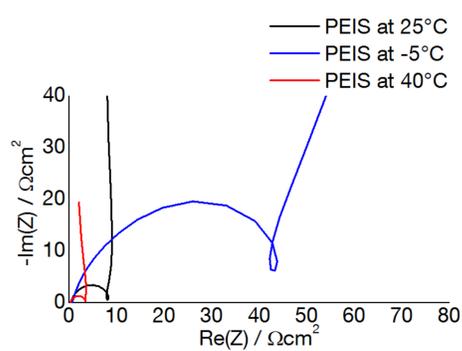


Fig. 4 PEIS at different temperatures. Internal resistance increases with temperature drop.

We compared half-cell measurements of LTO and LFP electrodes versus a lithium counter electrode, with both thin and thick electrodes. Using potentiostatic electrochemical impedance spectroscopy (PEIS) and galvanostatic cycling procedures, we can show differences in the charge transfer resistance and the capacity for thin and thick electrodes as seen in Fig. 7. After a temperature treatment, we can see changes in both, resistance and capacity (Fig. 4). According to a publication by Allen and Wolfenstein^[6], smaller particles of the active material provide better capacities at low temperatures. Therefore, we break the big particles via ball milling, using a planetary mill. Fig. 6 shows both original and ball milled particles.

We built full-cells of matching thin and thick electrodes with a combined active material mass in the order of about $1 \text{ mg}_{\text{active mass}}/\text{cm}^2$ and $10 \text{ mg}_{\text{active mass}}/\text{cm}^2$, respectively. Although the charge transfer resistance (CTR), as seen in Fig. 7, in thicker electrodes is smaller. Thick electrodes provide inferior capacities at faster charge/discharge rates compared to thin ones (see Fig. 5 and Fig. 9). This is due to a diffusion limitation inside the porous electrode. Here, we will try a calender for better compression, and therefore contact, of the coating.

Nonetheless, with a thick electrode full-cell we get a constant capacity for more than 3,000 deep cycles (Fig. 8).

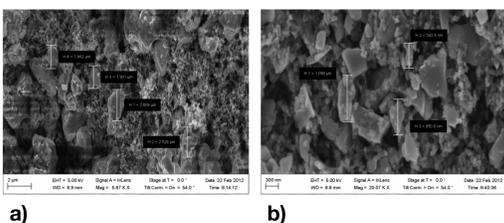


Fig. 6
a) SEM picture of an untreated LTO electrode. The particle size is between 1 and 3 μm .
b) Ball milled particles, coated as an electrode. Here, the particle size is between 1 μm and 500 nm.

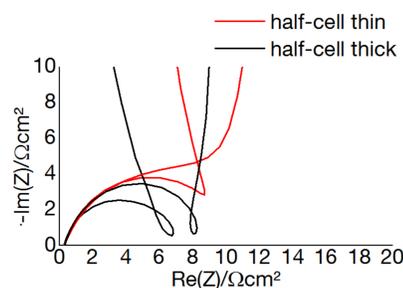


Fig. 7 PEIS of thin and thick LTO half-cells. While high frequency resistances are alike, CTR of thick electrodes is smaller.

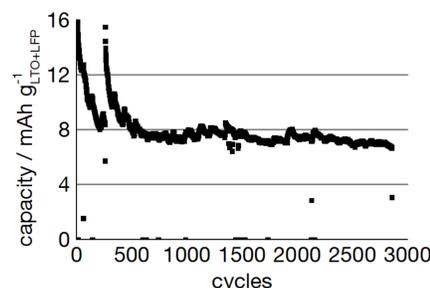


Fig. 8 Constant capacity of LTO/LFP full-cell for 3,000 deep cycles with a charge/discharge rate of 1C.

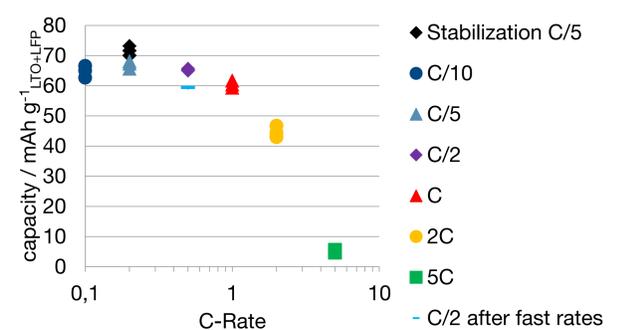


Fig. 5 Discharge capacities of a thin LTO/LFP full-cell with $4 \text{ mg}_{\text{active mass}}/\text{cm}^2$ at different C-Rates at room temperature.

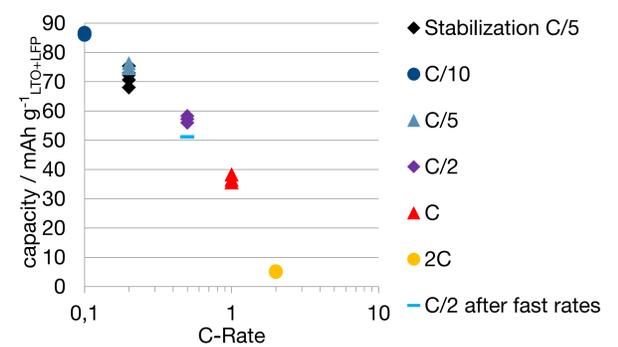


Fig. 9 Discharge capacities of a thick LTO/LFP full-cell with $17 \text{ mg}_{\text{active mass}}/\text{cm}^2$ at different C-Rates at room temperature.

Outlook

The results show that our full-cells possess a stable capacity for 3,000 cycles and more. All types of electrodes have an excellent reversibility and electrodes with thinner coatings have a better capacity over a wide range of charge/discharge rates. Due to this fact, we will focus our future measurements on the behavior of electrodes with low weight density. The electrodes will be improved by heated calendaring to compress the electrode coating. A long-term energy storage system needs to obtain a stable capacity over a long time at different ambient conditions. According to the cited literature,

smaller particles show a better cycling behavior at low temperatures. We also expect a higher cycling efficiency due to a lower charge transfer resistance. Therefore, we'll scale down the LTO particles from approximately $2.5 \mu\text{m}$ to about $0.5 \mu\text{m}$ by planetary ball milling. For long-term cycling tests, we are trying different conductive additives to avoid electrolyte decomposition at high temperatures and to minimize side reactions. In earlier tests this lead to destruction of the electrode material due to reactions with the conducting LiPF_6 -salt.