Sensitivity of positrons to anionic redox in Li-rich Li-ion battery cathode materials

Jan Kuriplach[1,*] and Bernardo Barbiellini[2,*]
[1]*Charles University, Prague, Czech Republic*
[2]*LUT University, Lappeenranta, Finland*

*email: Jan.Kuriplach@mff.cuni.cz and Bernardo.Barbiellini@lut.fi

Nowadays, Li-ion batteries (LIBs) are the subject of intensive investigations. The main reason consists of applying LIBs to energy storage. Thus, it is highly desirable to understand the underlying physical principles in order to be able to improve battery usage parameters. In efforts to increase the battery capacity, Li-rich materials containing more than one Li atom per formula unit are being investigated. In standard LIBs, cationic redox plays an important role. For example, in batteries based on the $LiFePO_4$ cathode the cationic redox pair is Fe^{2+}/Fe^{3+} (corresponding to discharged (fully Li loaded) / charged (Li unloaded) cathode). This means that upon discharging, Li atoms are coming to the cathode and give their electrons to Fe ions. On the other hand, in Li-rich LIBs, the anionic redox complements (or even replaces) the cationic one. In this way, some O^{2-} ions may become O^{1-} during charging (Li is leaving the cathode). A typical example is Li_2MnO_3 where Mn cationic redox reaction (Mn^{4+}/Mn^{5+}) is supposed to be impossible and where the anionic redox has been proven experimentally [1,2].

Since the valence of some oxygen ions in in Li-rich LIBs is supposed to be (nominally) -1 in comparison to -2 valid for most of other oxides, the positron distributions around oxygen ions should differ – because O^{1-} will become less attractive for positrons – and in principle this should be detectable via positron annihilation spectroscopy. The electron-positron momentum distribution should give clear signature of this effect [3,4], but in this contribution, we concentrate on the positron distribution and related positron lifetime in order to evaluate and understand the expected effect of anionic redox from the theoretical viewpoint based on the density functional theory (DFT). The studied systems are selected oxides from the series $LiMO_2$ and Li_2MO_3 with M being a transition metal (as inspired by a recent study [5]). In addition, we examine $Li_{1.2}Ti_{0.4}M_{0.4}O_2$ system being a candidate for a high-capacity Li-rich LIB [6]. Since the electronic structure of studied materials depends to some extent on the approach chosen to the electron exchange-correlation functional, we explore several commonly used DFT approximations. Along with the study a brief overview of recent PAS activities in the LIB field is given.

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