Abstract

We propose a new two-step synthesis with which we were able to prepare $LiMnPO_4$ particles (∼20–50 nm) that are embedded in conductive carbon matrix (14 wt. % of carbon). The synthesized $LiMnPO_4$-based cathode material showed a high specific capacity of ∼160 mA h g^{-1} at 55 °C (rate of C/20) and ∼155 mA h g^{-1} at 25 °C (using the CC−CV mode of battery cycling). We have demonstrated a long-term cycling (almost 2 years) with very good stability (the average capacity decay was less than 0.06 % per cycle). After about 500 cycles a sudden capacity drop was observed. Degradation processes in various stages of cycling were thoroughly examined using a range of techniques. Severe surface film formation, manganese dissolution and degradation of Li_xMnPO_4 which is accompanied by the formation of $Li_4P_2O_7$ were clearly identified. The good long term stability seems to be due to small particles that are coated with dense, protective carbon coating. Decomposition is most likely initiated at local defects in the microstructure of pyrolytic carbon coating around $LiMnPO_4$ particles. In addition to known degradation mechanisms of $LiMnPO_4$ we observed changes in morphology of the carbon black additive and pronounced gradual amorphization of $LiMnPO_4$ active material, which was also confirmed with HRTEM and XRD analysis.

Keywords: two step synthesis, $LiMnPO_4$, lithium ion batteries, long term cycling, degradation.