Abstract No. 2704

Synthesis and Processing of Oxygen Rich Lithium Manganospinel films For Robust Rechargeable Microbatteries

Deepika Singh[a]*, Heinrich Hofmann*, Won-Seok Kim†, Valentin Craciun†, Rajiv K. Singh†

[a]Sinmat Inc., GTEC Center, Gainesville, Florida-32641.
*Powder Technology Laboratory (LTP), Department of Materials Science, Swiss Federal Institute of Technology (EPFL), CH 1015 Lausanne, Switzerland.
†Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA

Significant effort in the past decade has been devoted to develop robust bulk rechargeable batteries for computers, communication and electric vehicle applications. There is a growing demand for solid state microbatteries particularly to power MEMS devices such as pumps motors, valves and sensors. In space, these batteries could energize a platform of nanosatellites, while on earth they could enable tiny patches worn directly on the skin to monitor medical conditions (blood sugar, arterial oxygen etc.). The efforts were mainly focused on developing rechargeable battery systems, which exhibit high capacity, long cycle life and high discharge rate capabilities. $LiMn_2O_4$ based cathodes have been researched extensively as they are not only economical but also environmentally desirable. Research includes composition and doping variation, formation of novel phases and microstructural tailoring but none of the material modifications have successfully satisfied all the above mentioned performance criteria. In this paper we show a correlation between processing parameters, microstructure and electrochemical performance of the Li-Mn-O cathode films. In addition we discuss the formation of metastable oxygen-rich lithium manganospinels $Li_{1-\delta}Mn_{2-2\delta}O_4$, using a unique ultraviolet assisted deposition process. These defective films exhibit high capacity (> 230 mAh/gm), long cycle life (less than 0.05 % capacity loss per cycle for 700 cycles), and high discharge rates (> 25 C for 25 % capacity loss). The long cycle life and high capacity was attributed to the ability to cycle the Mn^+ valence to less than 3.5 without onset of Jahn-Teller structural transformation, while the high discharge rate was attributed to the extremely high diffusivity of Li^+ in the defective $Li_{1-\delta}Mn_{2-2\delta}O_4$ phase.

Although it has been speculated that the oxygen rich lithium maganospinel such as $Li_2Mn_4O_9$ can deliver high steady capacities in excess of 150 mAh/gm, the reproducible synthesis of fully oxidized single phase using bulk solid state chemistry technique is quite difficult. Increased oxygen incorporation has particularly been difficulty as higher processing temperature reverts the defective spinel back to the $LiMn_2O_4$ form. We have used an ultraviolet assisted pulsed laser deposition process to synthesized $Li_{1-\delta}Mn_{2-2\delta}O_4$ films on various substrates which demonstrate excellent electrochemical characteristics. In this process an ultraviolet lamp emits significant radiation at 182 nm which helps to break the oxygen in the deposition chamber into atomic and other reactive species such as ozone. The enhanced reactivity of non-equilibrium oxygen species leads to formation of $Li_{1-\delta}Mn_{2-2\delta}O_4$ films during the UVPLD process. Microstructural measurements (XRD, RBS, XPS) conducted by us confirmed the formation of the oxygen rich magneto-spinel. Rutherford backscattering spectrometry (RBS) and NRA (Nuclear Radiation Analysis) confirmed that composition stoichiometry of Li/Mn was approximately 0.5. X-ray photoelectron spectroscopy (XPS) also indicated that the ratio of O/Mn was in the range of 2.2 ± 0.1 for UVPLD films with a corresponding enhancement in the Mn^{4+}/Mn^{3+} ratios.

Extensive electrochemical measurements(CV and AC impedance) were conducted on the $LiMn_2O_4$ and $Li_{1-\delta}Mn_{2-2\delta}O_4$ films. The redox peaks from the cyclic voltammograms were used to estimate the lithium ion diffusivity using the Randle-Sevick equation. Diffusivity values of $5.0 \times 10^{-7} \sim 2 \times 10^{-8}$ cm^2/sec were obtained from $Li_{1-\delta}Mn_{2-2\delta}O_4$ films, which was 1 ~2 order of magnitude higher than the diffusivity values obtained from spinel $LiMn_2O_4$ films. Figure 1 shows the cycle life of the $Li_{1-\delta}Mn_{2-2\delta}O_4$ films. This figure shows that the initial total capacity of $Li_{1-\delta}Mn_{2-2\delta}O_4$ is approximately 232 mAh/gm. The capacity loss after 1500 cycles is less than 5 %, which translate to a loss of 0.05 % per cycle. Discharge rate effects were also measured Results indicate that if the microstructure and the film thickness are carefully tailored, very high rate discharge capability (10-50C)are obtained. In conclusion we have demonstrated that the synthesis of defect Li-Mn-O thin films by UVPLD method provides excellent unmatched battery characteristics for potential applications in consumer electronics, energy storage, and automobile applications.

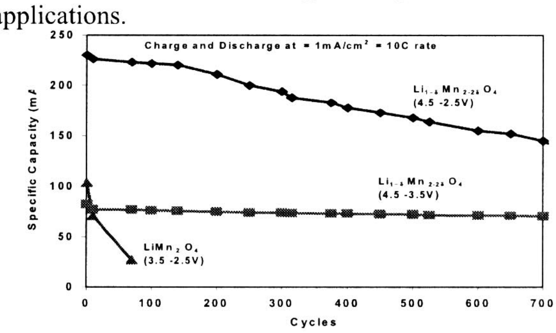

Fig 1: Cycle life of the $Li_{1-\delta}Mn_{2-2\delta}O_4$ films.

1. M. M. Thackeray, *J. Electrochem. Soc.*, **142**, 2568 (1995).
2. M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, **18**, 461 (1983).