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The 2009 Edward G. Weston Summer Research Fellowship — Summary Report

High Precision Charger to Investigate Spinel $Li_{1+x}Mn_{2-x}O_4$ at Elevated Temperatures

by Shu-Lei Chou

In order to meet the requirement of the power source for electrified vehicles (hybrid (HEV), plug-in hybrid (PHEV), extended-range electric (EREV) and all-electric (EV)), advanced lithium-ion batteries with better cycle life (up to 3000 cycles), safety, and lower cost are required. Comparing the existing promising cathode materials including $LiCoO_2$, $LiFePO_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, spinel structure lithium manganese oxide ($LiMn_2O_4$) is the cheapest one and with relative lower toxicity and higher safety.[1,2] Researchers have paid great efforts to improve the performance of $LiMn_2O_4$ spinel as a cathode material for rechargeable lithium-ion batteries. Nowadays, $LiMn_2O_4$ based batteries have shown very good performance at room temperature. However, at elevated temperatures they are suffering from bad cycling stability. In order to improve the performance at elevated temperature, typically, there are three major ways, including doping other elements (Li, Al, Co, Ni, Cu, Zr), coating a protective layer, and adding additives to the electrolyte.

On the other hand, it is not practical for the university researcher to make a total lithium-ion cell and to cycle up to 3000 cycles for every sample. Here we use a new system named High Precision Charger (HPC) designed and assembled in our group to evaluate the as-prepared $LiMn_2O_4$ spinels. The capacity loss is due to the undesired reactions in Li-ion batteries, which can consume or produce charge at either the positive or negative electrode. So if we can accurately measure coulombic efficiency on the order of 0.01% via our HPC, we should be able to tell the impact of trace impurities, additives, coatings, etc. in only a few charge-discharge cycles. The detail of this HPC system can be found elsewhere.[3]

Here, a series of $LiMn_2O_4$ spinels with excess amount of Li were prepared by a typical solid-state reaction route. The method used here is a solid state method adopted from the literature.[4] Typically, $Li_{1+x}Mn_{2-x}O_4$ (x = 0, 0.05, 0.1, 0.15, and 0.2 named as M1, M2, M3, M4, and M5, respectively) was synthesized via a two step heating procedure in air using the mixture of desired amount of Li_2CO_3 (Alfa Aesar, 99.0%) and $MnCO_3$ (Erachem Comiloy Inc., 99%). The mixture was heated to 650°C for 20 h in air, and mixed and heated at 750°C for 20 h again. Figure 1a shows the X-ray diffraction (XRD, D5000 Siemens) patterns of the as-prepared samples. It can be seen that the samples show cubic structure with a space group of Fd-3m. The lattice

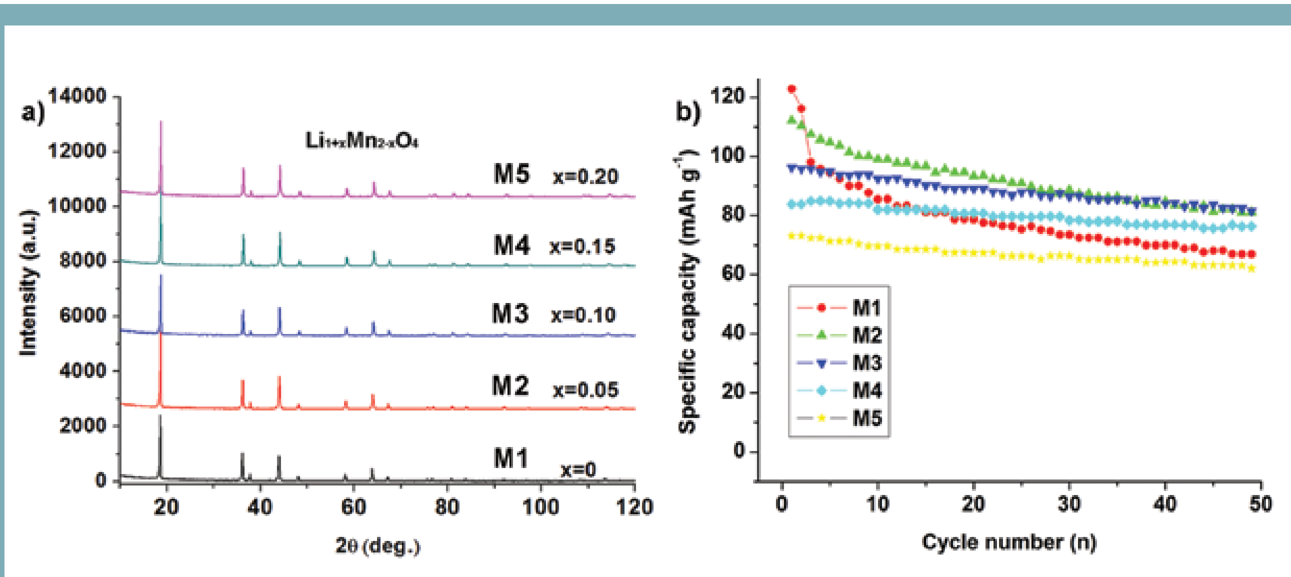

Fig. 1. *(a.) XRD patterns of $Li_{1+x}Mn_{2-x}O_4$ samples; (b.) Cycle life of the electrode containing $Li_{1+x}Mn_{2-x}O_4$ serials samples between 3.0 and 4.3 V vs Li/Li^+ at 55°C.*

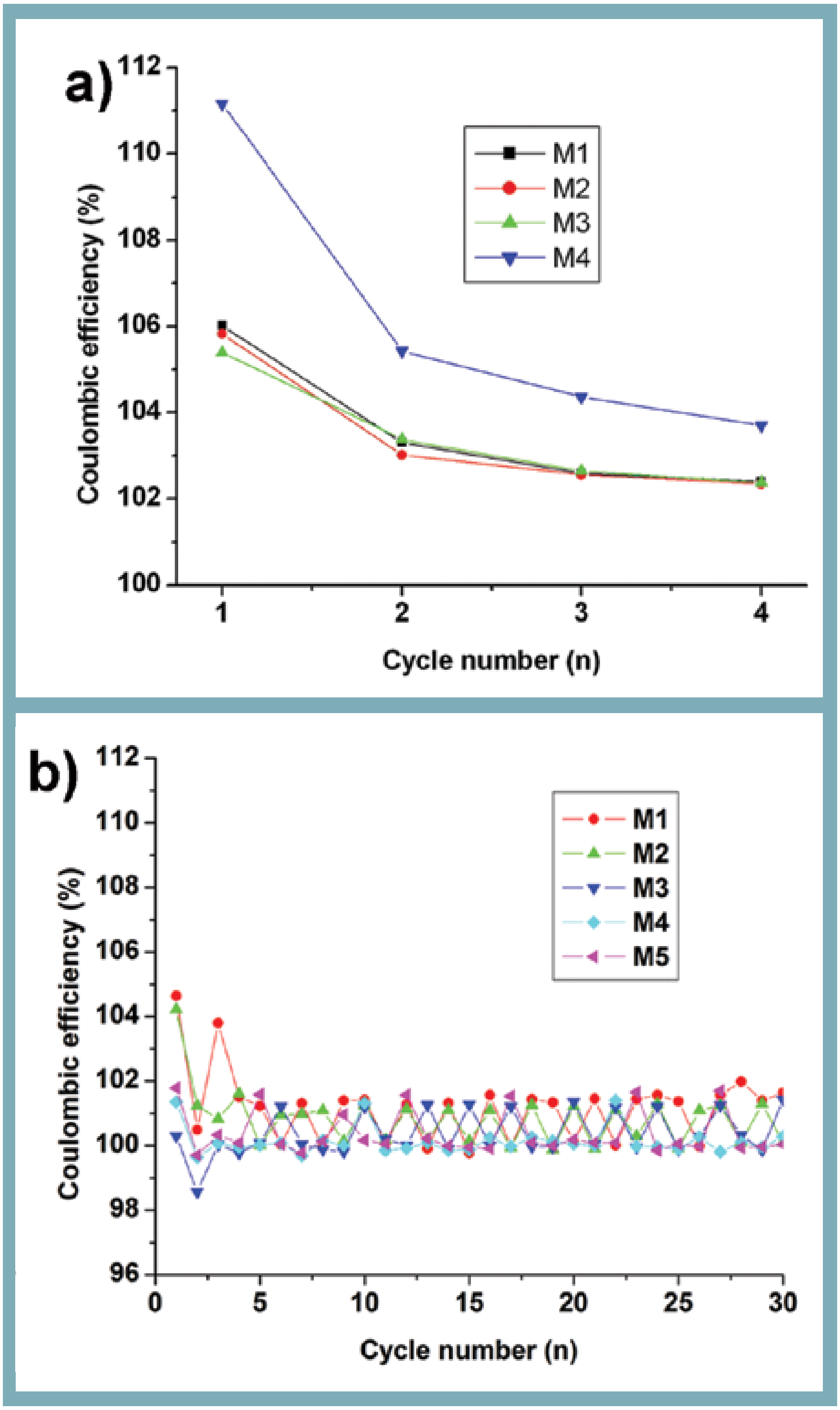

Fig. 2. *Coulombic efficiency obtained from (a.) the High Precision Charger and (b.) the Moli charger system.*

constants *a* of M1 to M5 are calculated to be 8.2422, 8.2265, 8.2113, 8.2013, and 8.1931Å, respectively. To test the electrochemical performance, the electrochemical cells (2325 coin-type cell) contained working electrode ($Li_{1+x}Mn_{2-x}O_4$: PVDF: Super-S carbon = 90:5:5), a polypropylene microporous separator (Celgard 2500), 1 M $LiPF_6$ in ethylene carbonate: diethyl carbonate (EC: DEC = 1:2 vol) electrolyte (Mitsubishi Chemical), and lithium metal foil as counter and reference electrode. All cells were assembled in an argon-filled glove box and tested at a constant temperature of 55±1°C. The cells were cycled between 3.0 and 4.3 V using Moli charger system at a current of 0.05 C for the first 2 cycles and a current of 0.2 C for the following cycles. Figure 1b shows the cycle stability of the as-prepared samples. It can be seen that the capacity retention can be improved by doping excess lithium in the spinel structure.

Figure 2a shows the preliminary High Precision Charger results. The HPC gives better resolution than the Moli charger system (Figure 2b). The as-prepared $Li_{1+x}Mn_{2-x}O_4$ samples show coulombic efficiencies around 102%, indicating the bad cycle stability for long cycles. Further testing is still underway. Different coating and different additives will be investigated using HPC to further improve the performance.

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