

Fabrication and Electrochemical Study of a Binder-Free LiMn_2O_4 Cathode

by Sau Yen Chew

L iMn_2O_4 spinel has the potential to replace LiCoO_2 as the cathode material used in lithium-ion (Li-ion) batteries because of its low cost, low toxicity, stable structure for Li-ion extraction, and a rather high charge density.¹⁻² However, LiMn_2O_4 spinel has poor electronic conductivity.¹ In general, carbon black and PVDF binder are mechanically mixed with the oxide to solve this problem. This simple preparation method may not easily deposit carbon black onto every single surface of the electro-active particles, especially when nano-sized LiMn_2O_4 is applied. In fact, strong fading is always observed for nanostructured LiMn_2O_4 electrode after prolonged cycling. This is probably due to the poor distribution of carbon black and binder, which will influence the electrochemical performance, since disconnection often leads to degradation of the electrode.

Here, a non-aqueous substrate-induced coagulation (SIC) method patented by Besenhard *et al.*³ is adapted to deposit carbon black uniformly onto nano-sized LiMn_2O_4 in a gelatin-like solution. The preparation route applied for this study has also been simplified. Basically, it consists of three steps.

Step 1. the surface of flame-made LiMn_2O_4 nanoparticle⁴ is coated with a thin layer of polyelectrolyte (polyvinyl alcohol, PVA 7200 Fluka) by adding 125 mg nano-sized LiMn_2O_4 into 5 mL of 0.2 wt% PVA/*N*-methyl-2-pyrrolidinone (NMP) solution. Subsequently, this dispersion is ultrasonicated for 15 min and stirred for another 24 h.

Step 2. The PVA-coated LiMn_2O_4 dispersion is then added to a known amount of metastable carbon black (Ensaco 350, TIMCAL SA) solution, where the stability has been adjusted with the addition of 0.02 mol L^{-1} LiCl in NMP solvent.

Step 3. The carbon black-coated LiMn_2O_4 suspension (solution of Step 2.) is then doctor-bladed onto an aluminum foil at a thickness of 150 μm and dried under vacuum at 110°C for overnight. Electrodes with a diameter of 13 mm are punched out after drying. Finally, binder-free LiMn_2O_4 electrodes are obtained.

Figure 1 shows electrochemical properties of the binder-free LiMn_2O_4 electrode. The $\text{LiLiMn}_2\text{O}_4$ half-cells is first charged (Li^+ extraction) at a specific current of 148 mA g^{-1} to 4.3 V, followed by discharging (Li^+ insertion) to 3.5 V. Figure 1a shows that the

coulombic efficiency of the cell is kept at approximately 100% after 30 cycles, suggesting high reversibility in the Li-ion extraction and insertion processes. In addition, cyclic voltammogram of the cell (refer inset of Fig. 1a) reveals two pairs of symmetrical redox peaks, which are characteristics of the

LiMn_2O_4 spinel.⁴ Meanwhile, Fig. 1b shows the high rate capability of the binder-free LiMn_2O_4 electrode upon cycling, with charge retention above 55 mAh g^{-1} (equivalent to > 75% of the galvanostatic Li^+ insertion, from inset of Fig. 1b) when cycled at 40 C-rate over 80 cycles.

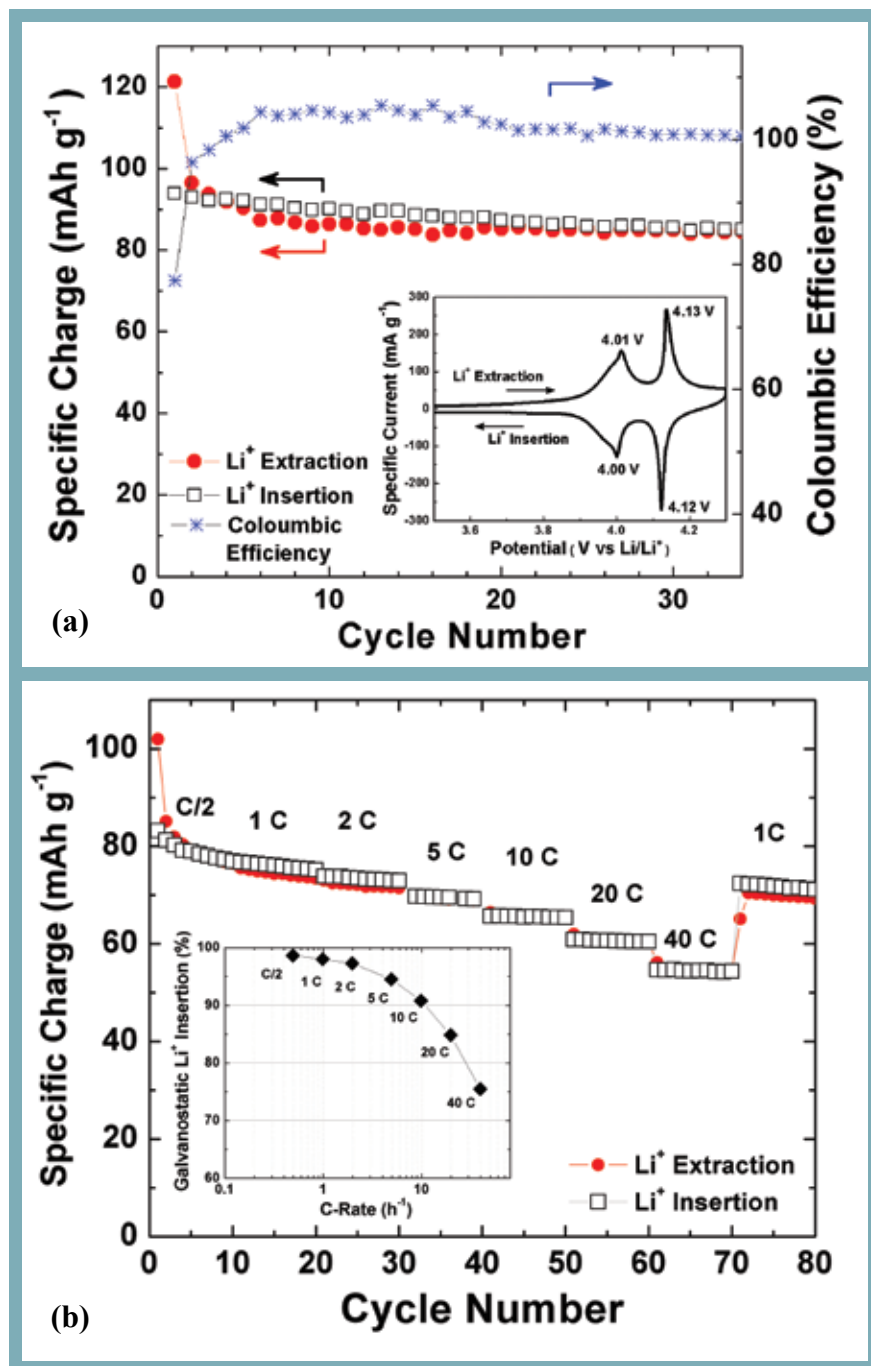


FIG. 1. (a) Galvanostatic Li^+ extraction (charge) and insertion (discharge), and the corresponding coulombic efficiency profiles of nano-sized LiMn_2O_4 electrode at 1C-rate with inset showing the 1st cycle cyclic voltammogram at a scan rate of 0.05 mV s^{-1} ; (b) Rate capability of the nano-sized LiMn_2O_4 electrode with inset showing the galvanostatic Li^+ insertion, given as a percentage of the total Li^+ insertion that includes the potentiostatic step, plotted against the C-rate. A 1C-rate is assumed to be 148 mA g^{-1} and the specific charge is based on the mass of LiMn_2O_4 in the electrode.

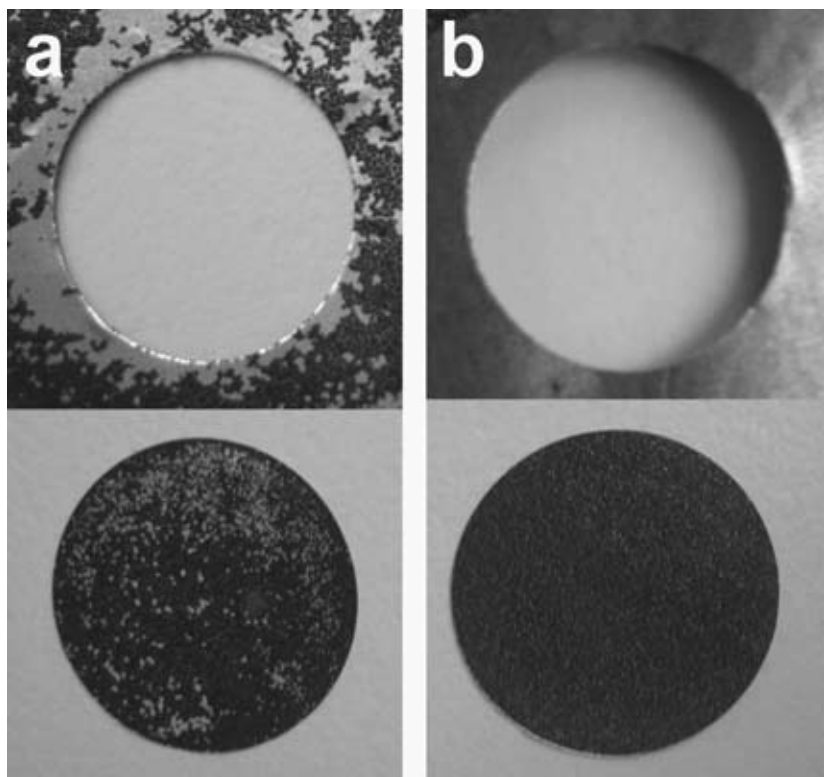


FIG. 2. Photographs of punched-out electrodes of the (a) conventional-made LiMn_2O_4 -carbon black-PVDF, and the (b) SIC-made LiMn_2O_4 -carbon black. The electrode diameter is fixed at 13 mm.

It is also noteworthy that good mechanical integrity within the electrode with respect to the current collector is also achieved (see Fig. 2). Hence, the flexibility of the electrode is improved and LiMn_2O_4 can be handled easily during the cell assembly. In summary, this study shows that binder-free LiMn_2O_4 cathodes with stable charge and good mechanical properties can be obtained using our modified SIC method. ■

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