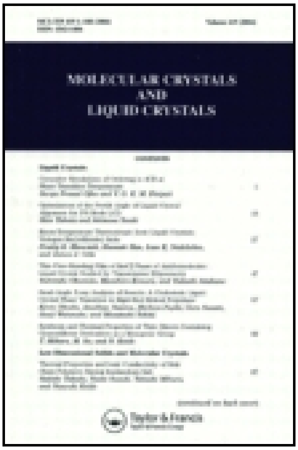

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# Enhanced Electrochemical Properties of Li Secondary Batteries Using Polypyrrole/$LiMn_2O_4$ Composite Cathodes

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# Enhanced Electrochemical Properties of Li Secondary Batteries Using Polypyrrole/$LiMn_2O_4$ Composite Cathodes

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Polypyrrole(PPy)/$LiMn_2O_4$ composites were prepared by chemical oxidation of pyrrole onto $LiMn_2O_4$ with dodecylbenzene sulfonate as a dopant. The polymerization occurred mainly on the surface of $LiMn_2O_4$ to yield the entirely coated $LiMn_2O_4$ particles. The capacity of the cell reached the maximum of 124 mAh/g at 4.1 wt% of PPy in the active material. The composite cell showed enhanced charge-discharge properties compared with a pure $LiMn_2O_4$ cell. The PPy may enhance the electron exchange ability and stabilize the structure of $LiMn_2O_4$.

Keywords  $LiMn_2O_4$; polypyrrole; composite; cathode; Li battery

## INTRODUCTION

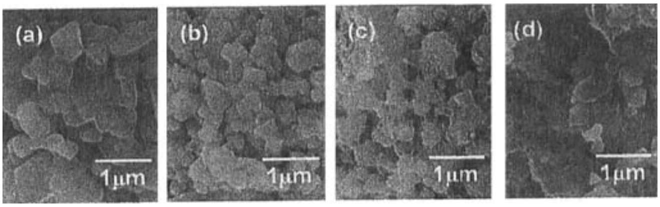
Spinel $LiMn_2O_4$ has been extensively studied as one of the most promising cathode materials of lithium secondary batteries. It is easier to prepare, less expensive, and less toxic than other metal oxides such as $LiCoO_2$ and $LiNiO_2$. In this paper we report further improvement of the capacity and the charge-discharge performance of Li ion cells by fabricating polypyrrole (PPy)/$LiMn_2O_4$ composite as a cathode material.

## EXPERIMENTAL

$LiMn_2O_4$ powders were coated by the chemical oxidation of pyrrole in an aqueous solution containing dodecylbenzene sulfonic acid, sodium salt as a dopant. Coated $LiMn_2O_4$ powders (composites) and graphite conductor were dispersed in a 6 wt% PVDF/NMP solution, which was dip-coated onto an extended Al grid and dried at 80 °C in a vacuum oven for 24 hours to yield cathodes. The Li/($LiMn_2O_4$ or PPy/$LiMn_2O_4$) ion cell with EC/DMC/ $LiPF_6$ was enclosed in a plastic bag by a vacuum sealer.

## RESULTS AND DISCUSSION

As shown in Figure 1, the increment of PPy content in the composite yielded the thickening of a rough skin of PPy that covered the extremely smooth surface of pure $LiMn_2O_4$, which implies that the polymerization of pyrrole occurred mainly on the surface of $LiMn_2O_4$.



$\sigma = 6 \times 10^{-6}$ S/cm $\sigma = 1 \times 10^{-4}$ S/cm $\sigma = 1 \times 10^{0}$ S/cm $\sigma = 4 \times 10^{0}$ S/cm

FIGURE 1 SEM image and dc conductivity of PPy/$LiMn_2O_4$ composite containing (a) 0, (b) 4.1, (c) 8.4, and (d) 21.5 wt% of PPy.

The higher content of PPy resulted in the higher dc conductivity of the composite powders, and the composite containing 21.5 wt% of PPy yielded the conductivity of 4 S/cm, almost equal to that of PPy doped with DBSA anions (15 S/cm) indicating that the PPy effectively formed a conduction path within the composite powders by coating the entire surface of the $LiMn_2O_4$ particles [1].

As shown in Figure 2, the cell fabricated with a cathode containing 4.1 wt% of PPy in the active material exhibited the highest discharge capacity of 124 mAh/g. Such an increase in capacity might result from the enhanced electron exchange ability between PPy and $LiMn_2O_4$, which promoted the utilization of $LiMn_2O_4$. For the cathode containing only graphite conductors, partial or point contacts are expected. Since the electron exchange is limited to the contact region, the utilization of $LiMn_2O_4$ is less than that of the PPy/$LiMn_2O_4$ [2]. However, the higher content of PPy reduced the capacity of the cell because the specific capacity of PPy is lower than that of $LiMn_2O_4$.

The cell assembled with a cathode containing 4.1 wt% of PPy in the active material exhibited good charge-discharge performances after 50 cycles at room temperature as shown in Figure 3. The cell fabricated with pure $LiMn_2O_4$ showed serious capacity fading after 30 cycles. EVS

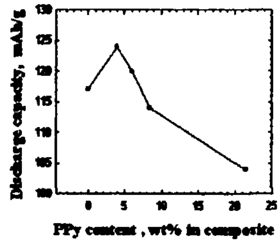


FIGURE 2 Initial discharge capacity of cells as a function of PPy content.

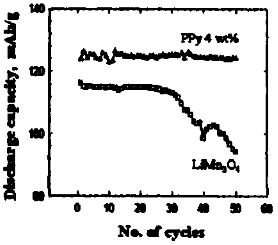


FIGURE 3 Discharge capacity of cells as a function of number of cycles.

profiles shown in Figure 4 indicate that the capacity fading resulted from the poor reversibility of typical $LiMn_2O_4$, which might be caused by the $Mn^{3+}$ dissolution or the volume change of Mn spinel during cycling test. On the other hand, EVS profiles of $PPy/LiMn_2O_4$ cell changed little with cycling at potential range of 4.2V indicating the good reversibility of $PPy/LiMn_2O_4$. It is believed that the PPy stabilized the $LiMn_2O_4$ spinel structure during the charge-discharge process by limiting the direct contact between $LiMn_2O_4$ and electrolyte solution to reduce the $Mn^{2+}$ dissolution.

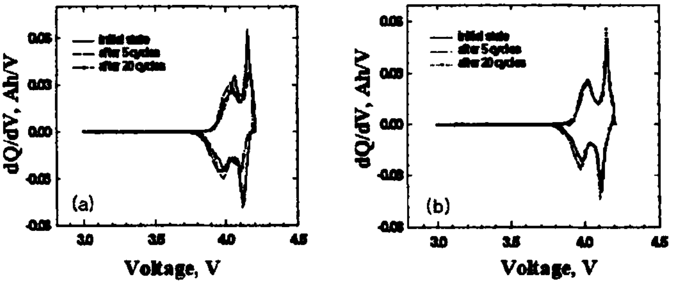


FIGURE 4 Electrochemical voltage spectroscopy profiles of a cell containing (a) 0 and (b) 4.1 wt% of PPy content in the active material.

## Acknowledgment

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