



Short communication

Electrochemical performance of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material

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ABSTRACT

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was prepared by sol–gel method and annealed at 850°C for 15 h. The prepared powder was coated with ZnO by dissolving zinc acetate in methanol and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powder was mixed in this solution followed by the continuous stirring for 4 h. The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powder was structurally characterized using X-ray diffraction and scanning electron microscopy (SEM). The coin cell was fabricated using ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as cathode materials, LiPF_6 , dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 wt ratio) as electrolyte, and Li foil as anode. It was found that ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode materials had the initial discharge capacity of about 146 mA h g^{-1} . The discharge capacity retention after 50 cycles was found to be nearly 97%.

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1. Introduction

During past few years, an even increasing demand for portable electronic devices, computers, digital camera, and eventually, hybrid vehicles has given rise to the increased production of Li ion rechargeable batteries to provide the required power sources [1–3]. Since Li ion batteries have the highest energy density per weight or volume among all available rechargeable batteries, these are considered to be the most suitable candidates for most electronic devices. For the last two decades lithium intercalated compounds such as LiMn_2O_4 , LiCoO_2 , and LiFePO_4 are being used as cathode materials for the Li ion rechargeable batteries [4–6]. Some of these materials suffer with poor cycle life and a few are toxic. Wei et al. [7] synthesized $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 0.5$) and studied the evolution of the local structure and its electrochemical properties. They found that $\text{LiMn}_{1.8}\text{Ni}_{0.2}\text{O}_4$ has the most compact $[\text{Mn}(\text{Ni})\text{O}_6]$ octahedron and the strongest $\text{Mn}(\text{Ni})=\text{O}$ bonds among all $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ compounds. They also observed that the electrolyte decomposition occurs above 4.8 V and becomes severe with Ni substitution. Singhal et al. [8] reported that $\text{LiMn}_{1.5}\text{Ni}_{0.46}\text{Rh}_{0.04}\text{O}_4$ cathode materials showed an initial discharge capacity of 153 mA h g^{-1} with the capacity retention of 93.5% after 50 charge–discharge cycles. It has already been reported by several researchers that the electrochemical performance of these lithium intercalated compounds can be

improved by various metal-oxide coatings, such as Li_2CO_3 , ZnO, MgO, SiO_2 , Al_2O_3 , SnO_2 , ZrO_2 , and SnO_2 [9–12].

Cho et al. [13] have reported that nanoscale coating of cathode materials with metal oxides (Al_2O_3 , ZrO_2 , etc.) improves the electrochemical performances, by suppressing lattice-constant changes during the first charge. Wang et al. [14] found that the surface modification of LiCoO_2 with MgO reduced the electrolyte decomposition and hence the cyclic performance of LiCoO_2 can be improved by MgO coating. Kim et al. [15] synthesized ZrO_2 -coated LiCoO_2 cathode material for Li ion battery. They found that ZrO_2 -coated LiCoO_2 cathode materials showed negligible capacity loss after 70 charge–discharge cycles at the cutoff voltage of 4.4 V, while bare LiCoO_2 exhibited 60% of its original capacity after only 30 cycles. The improved electrochemical behavior was attributed to suppression of cobalt dissolution by nanoscale metal-oxide coating. We have synthesized [16] phase pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders by chemical synthesis method. The cyclic voltammetric experiments showed the oxidation and reduction peaks corresponding to spinel LiMn_2O_4 as well as Ni^{2+} to Ni^{4+} oxidation and reduction peaks. Moreover, nickel was oxidized and reduced at higher voltage (4.862 and 5.05 V, respectively) in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, revealing its suitability for 5 V applications. The charge–discharge characteristics of this material showed improved cyclic performance. The initial discharge capacity of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was found to be about 140 mA h g^{-1} and after 50 charge–discharge cycles the discharge capacity retention was found to be about 94%. In the present work we report the structural and electrochemical properties of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material.

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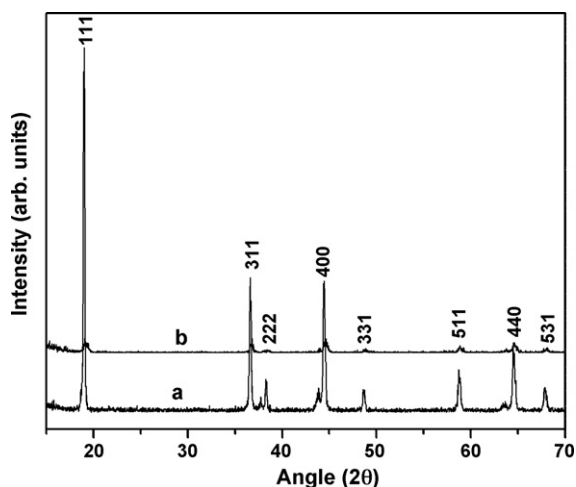


Fig. 1. XRD pattern of (a) the as-prepared $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and (b) ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode calcined at 850°C for 15 h.

2. Experimental

Lithium acetate [$\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$], manganese(II) acetate [$\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$], and nickel(II) acetate [$\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$] were procured from Alfa Aesar and used as precursor materials in their stoichiometric ratio. All the materials were separately dissolved in 2-ethylhexanoic acid with continuous stirring followed by heating at 80°C . After half an hour of heating, all solutions were mixed together followed by heating and continuous stirring up to boiling point for about half an hour. The solution was then kept for drying at about 100°C for 10 h, resulting in the formation of amorphous powders. The powder was grind and further dried at 400°C for 4 h to complete organic removal. Finally $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ phase was obtained at a calcined temperature of 850°C for 15 h. For coating of ZnO on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material, zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$] was first dissolved in ethanol and then $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode was mix in this solution followed by continuous stirring for about 4 h. Afterwards the solution was kept overnight for drying at 80°C . The resulting powder was then annealed at 400°C for 4 h, in order to complete organic removal and resulting into ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material. The crystallinity of the powder was confirmed from the XRD pattern of the sample, obtained using a Siemens D5000 X-ray powder diffractometer. The microstructure of the samples analyzed using scanning electron microscope (JOEL). The homogeneity of the ZnO coating was confirmed by X-ray mapping of the electrode using energy dispersive X-ray (EDX), coupled with scanning electron microscope. The cathode was prepared by mixing calcined cathode material, carbon black, and polyvinylidene fluoride in a weight

ratio of 80:10:10. *N*-Methyl pyrrolidone was used to make slurry of the mixture. The resulting slurry was casted onto aluminum foil followed by drying overnight at about 60°C in a vacuum oven. Li metal foil was used as the anode. Coin cells were prepared in an argon atmosphere inside a Glove Box (MBraun, USA) using $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ electrodes as cathode, Li foil as anode and lithium hexafluorophosphate, dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) as electrolyte. Cathode and anode were separated inside the coin cell using Celgard 2400 membrane. The thickness of the cathode was found to be about $90\ \mu\text{m}$. The electrochemical measurements (cyclic voltammetry and charge–discharge characteristics) were performed using Gamry Instruments potentiostat and PHE200 electrochemical software.

3. Results and discussions

Fig. 1 shows XRD patterns of the as-prepared $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and 2 wt% ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders. Both powders were confirmed to have a well-defined spinel phase with space group $Fd3m$. The XRD peaks corresponding to ZnO are not present in the diffractogram because of its low concentration. XRD patterns for the ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders produced some peak broadening without any impurity phases and the position of the diffraction lines shifted to the high angle side, implying that ZnO could exist as amorphous or nanosize.

Fig. 2 shows the scanning electron micrographs of the as prepared and ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders. It can be seen from scanning electron microscopy (SEM) pictures that the size of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles varies from 0.5 to $1\ \mu\text{m}$. For ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles, ZnO with particle size distribution of 10 nm or less was uniformly distributed on the surface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles. Fig. 3 shows the backscatter SEM, EDAX image of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ electrode as well as elemental maps of C, O, Mn, Ni and Zn. Carbon (c) comes from the carbon powder, used to make slurry of the cathode material. EDAX image shows the presence of Zn in the electrode. Mn map of the electrode shows a similar intensity distribution as Ni and O, indicating that all elements are homogeneously mixed in the electrode. It can be seen from the mapping of Zn that the Zn is uniformly coated onto the sample as there is no agglomeration and void region in the mapping of Zn. Similar type of observations were observed by Scheiba et al. [17] for the distribution of polymer electrolyte in proton exchange membrane fuel cells and Suresh et al. for the ZnO coating of $\text{Li}_{0.9}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_2$ cathode material [18].

Fig. 4 shows the cyclic voltammogram of the coin cell in 5 V range (voltage scan 3.5–5.2 V), measured at a scan rate of $0.1\ \text{mV s}^{-1}$. There are three anodic and cathodic peaks are observed for ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode material. The three pairs of

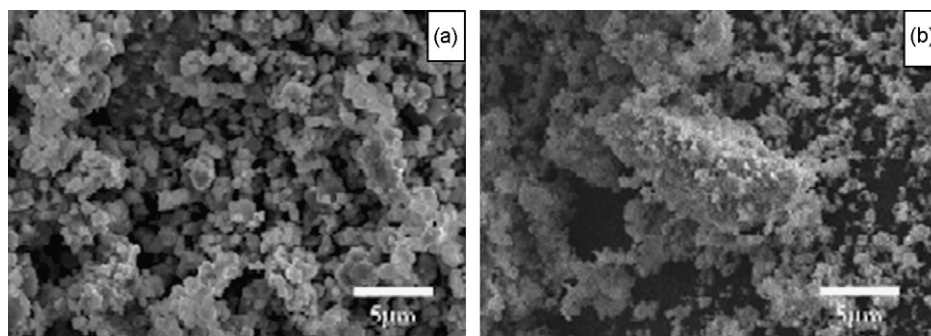


Fig. 2. SEM pictures of (a) the as-prepared $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and (b) ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ the cathode material.

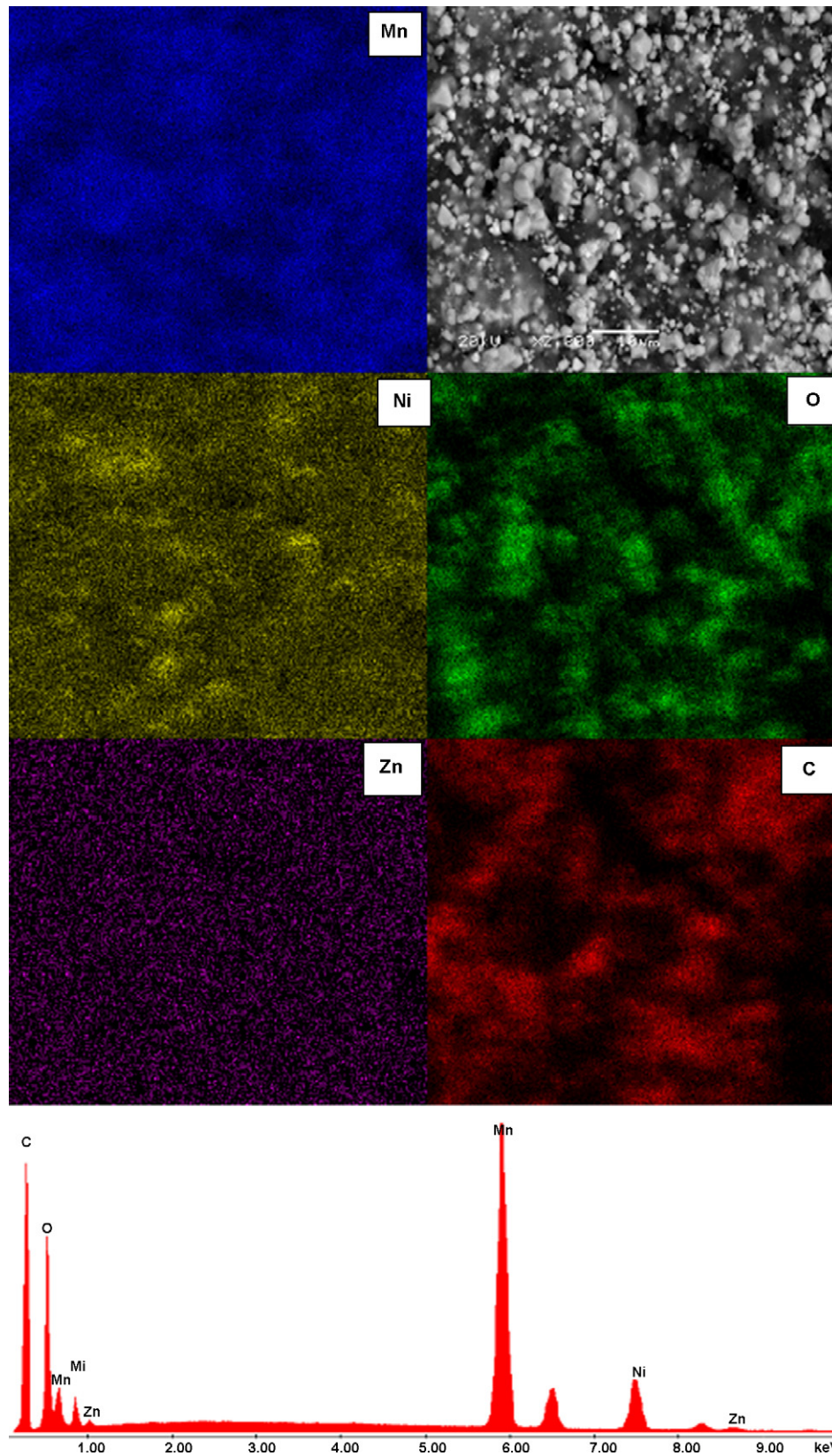


Fig. 3. EDAX and BSE micrographs of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ the cathode material and elemental maps for carbon (C), fluorine (Mn), platinum (Ni), oxygen (O) and zinc (Zn) for the same region, obtained by EDX mapping.

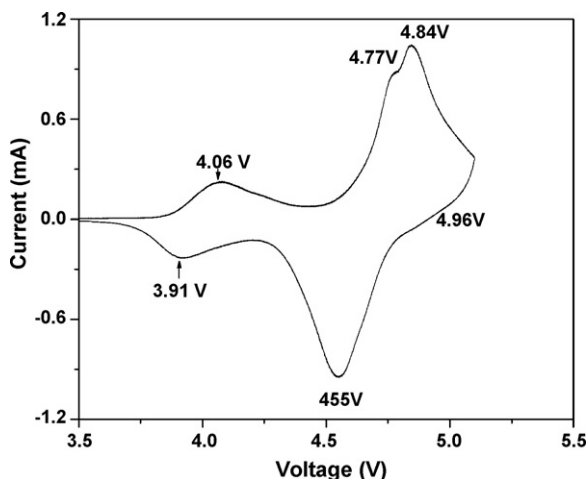


Fig. 4. Cyclic voltammety of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ /(EC + DMC)/Li coin cell in 3.5–5.3 V range at scan rate of 0.1 mV s^{-1} .

oxidation and reduction peaks for the spinel are corresponds to three-stage reversible intercalation/de-intercalation processes of lithium. The peak at 4.08 and 3.91 V corresponds to $\text{Mn}^{2+}/\text{Mn}^{3+}$ oxidation and $\text{Mn}^{3+}/\text{Mn}^{2+}$ reduction, respectively. The oxidation and reduction peak observed at 4.77 and 4.66 V is due to the oxidation of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and reduction of $\text{Mn}^{3+}/\text{Mn}^{4+}$, respectively. The voltammogram shows the reduction and oxidation peaks at 4.84 and 5.05 V, which corresponds to Ni^{2+} to Ni^{4+} reduction and oxidation peaks, respectively. This evidence suggested that in addition to manganese oxidation and reduction, nickel can also be oxidized and reduced at higher voltage in ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and hence can be operated at 5 V range in a coin cell. All these peaks are in quite agreement as reported earlier for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material [16] indicates that ZnO does not affect the electrochemical properties of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material.

Fig. 5 shows room temperature charge and discharge characteristics of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material in 5 V range (3.5–5.2 V). The initial charge and discharge capacity of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was found to be about 148 and 146 mA h g^{-1} , respectively. The columbic efficiency for first charge–discharge cycle was found to be about 98%. The initial charge and discharge capacity of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was found to be about 172 and 140 mA h g^{-1} , respectively [16]. The columbic efficiency for first charge–discharge

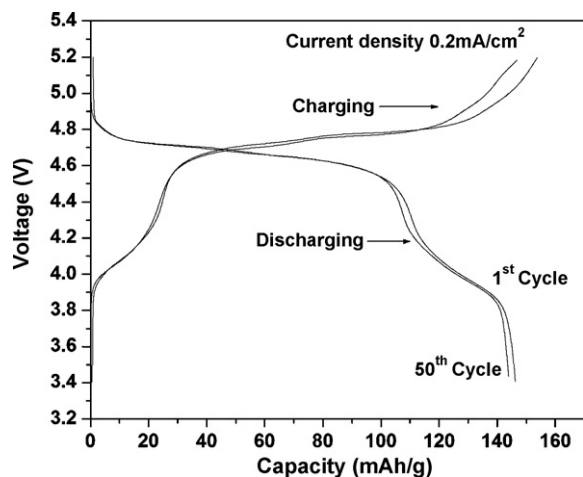


Fig. 5. Room temperature charge–discharge characteristics of 1st and 50th cycle of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ /(EC + DMC)/Li coin cell at 0.2 mA cm^{-2} between 3.5 and 5.2 V.

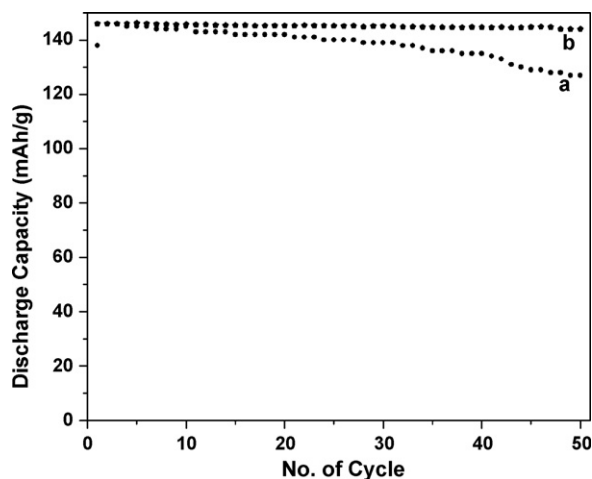


Fig. 6. Cycleability curve of (a) pure and (b) ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ the cathode material at a current density of 0.2 mA cm^{-2} .

cycle of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was 81%. The higher columbic efficiency observed in ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material may be the reason of initially higher (146 mA h g^{-1}) discharge capacity of the material as compare to uncoated sample (140 mA h g^{-1}) [16]. It is a well-known fact that HF contents play an important role for Mn dissolution in electrolyte [19]. Since ZnO works as HF collector hence the improved cyclic performance of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ may be due to the suppression of Mn dissolution into the electrolyte. Fig. 6 shows the cycleability curve of pure and ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material at a current density of 0.2 mA cm^{-2} . It can be seen from figure that capacity retention after 50 cycles for pure and ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was about 91 and 97%, respectively.

4. Conclusions

We have successfully synthesized ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material for application to Li ion rechargeable batteries. The X-ray diffraction pattern shows that the synthesized powder is phase pure and cyclic voltammogram studies revealed that ZnO coating does not affect the electrochemical behavior of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material. X-ray mapping of the electrodes shows the homogeneous coating of the Zn onto the cathode material. ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ showed improved discharge capacity of about 147 mA h g^{-1} as compared to pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material (140 mA h g^{-1}). After 50 charge–discharge cycles, the capacity retention of ZnO-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material was found to be about 97% at a discharge current density of 0.2 mA cm^{-2} .

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