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Structure and electrochemical performance of surface modified $LaPO_4$ coated $LiMn_2O_4$ cathode materials for rechargeable lithium batteries

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Abstract

$LiMn_2O_4$ spinel cathode materials were coated with 1.0, 2.0 and 3.0 wt% of $LaPO_4$ by the polymeric process, followed by calcinations at 800 °C for 6 h in air. The structure and electrochemical properties of the surface modified $LiMn_2O_4$ materials were characterized by XRD, SEM, XPS, cyclic voltammetry and charge–discharge techniques. XRD patterns of $LaPO_4$ coated $LiMn_2O_4$ revealed that the coating did not affect the crystal structure and space group Fd3m of the powder materials, compared to the uncoated $LiMn_2O_4$. XPS data illustrate that the $LaPO_4$ was completely coated over the surface of the $LiMn_2O_4$ core materials. 2 wt% of $LaPO_4$ coated $LiMn_2O_4$ cathode material exhibits specific capacity of 103 mAh/g (versus lithium metal) and excellent capacity retention (82% of its initial capacity) between 4.5 and 3 V after 100 cycles at elevated temperature (50 °C). $LiMn_2O_4$ coated with 0.0–3.0 wt% of $LaPO_4$ has slightly decreased the initial capacity, but the cycling stability increased remarkably over 3–4.5 V. This result indicates that the surface treatment should be an effective way to improve the overall properties of the cathode materials for lithium ion batteries. Among them, 2 wt% of $LaPO_4$ coated spinel $LiMn_2O_4$ cathode material has improved the structural stability, high reversible capacity at elevated temperature and excellent electrochemical performances of the rechargeable lithium batteries.

Keywords: Positive electrode materials; $LaPO_4$ coated $LiMn_2O_4$; XRD; XPS; Charge/discharge

1. Introduction

Increasing demand for reliable high energy density power sources has greatly intensified the research and development of lithium batteries. $LiMn_2O_4$ is a very promising cathode material with high capacity and medium cost for lithium batteries. $LiCoO_2$ has been mainly used for commercial applications due to its superior electrochemical stability compared to other cathode materials. But the major disadvantages are high cost, toxicity and low capacity [1]. Layered $LiNiO_2$ and spinel $LiMn_2O_4$ were recommended for the representative cathode materials for lithium batteries. However, the former has irreversible phase transitions during intercalation/deintercalation reaction and it is also very difficult to synthesize a stoichiometric $LiNiO_2$ [2,3]. The latter suffers from capacity fading during cycling, because the average Mn oxidation state becomes lower than 3.5 leading to a Jahn–Teller distortion of cubic to tetragonal transition [4]. Many researchers have made significant efforts to improve the electrochemical performances and stability of the cathode materials. Until now, there are two kinds of strategies. One way is substitution of heterogeneous atom into the host $LiMn_2O_4$ structure of cathode materials and the other one is surface modification. Several research groups have attempted to stabilize the structure of $LiMn_2O_4$ powders during cycling by substituting a small fraction of the manganese ions with several divalent or trivalent metal ions.

In order to solve this problem, surface modification of the cathode electrode materials are an effective way to reduce the side reactions. The surface treatment could decrease the surface area to retard the side reactions between the electrode and electrolyte and to further diminish the Mn dissolution

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during cycling. In literature report, the utilization of metal oxides [5–7] and organic/inorganic materials [8–10] for surface modification in both cathode and anode electrodes could improve the electrochemical properties of Li-ion battery. In Amatucci's report [11], lithium boron oxide was proposed as a proper surface treatment material for the cathode. In fact, lithium boron oxide has been widely studied as a solid lithium ionic conductor with good lithium ionic conductivity [12,13]. In addition, the molten lithium boron oxide with good wetting property and relatively low viscosity was provided for easy manufacturing even with small amount of coating materials [14]. The materials like Al_2O_3 [15–17], ZnO [18–20], TiO_2 [21,22], $AlPO_4$ [23–27], CeO_2 [28,29], MgO [30], $LiAlO_2$ [31] and MgF_2 [32] are coated to core materials, which enhanced the cycling behavior of the spinel $LiMn_2O_4$ cathode materials. In earlier studies, the polymer precursor method is involving the addition of a polymer to the reactant mixture, with the polymer acting as a capping agent which evaporates and decomposes away upon calcinations [33].

In this paper, we have attempted to synthesize $LaPO_4$ coated $LiMn_2O_4$ particles by the sol–gel method using polyvinyl alcohol (PVA) as a chelating agent. This method is facile and easy to control, without co-precipitating and gelling, or strict control of PVP concentration, pH of solution and varieties of metal salts. This long chain polymer (PVA) is highly dispersive and makes the material most reactive. It also acts as an excellent fuel to get high pure nano-crystalline powder with controlled stoichiometry. The cycling behaviors of $LaPO_4$ coated $LiMn_2O_4$ cathodes were evaluated with various discharge rates (0.5–20C rates) between 4.5 and 3.0 V. The effects of coating on the structural and electrochemical properties were investigated in detail.

2. Experimental details

2.1. Preparation of spinel $LiMn_2O_4$

$LiMn_2O_4$ powder was prepared by the sol–gel method; Li$(OCOCH_3)\cdot 2H_2O$ (AR 99.99% pure) and $Mn(OCOCH_3)_2\cdot 4H_2O$ (AR 99.98% pure) were dissolved in double distilled water with the mole ratio of Li:Mn = 1:2. It was then added to an aqueous solution of 1-M tartaric acid under vigorous stirring and the pH value of the solution was adjusted to 6–7 by adding aqueous ammonia. The resulting solution was evaporated at 80 °C until the formation of transparent gel. Finally, the gel precursor was decomposed at 300 °C for 8 h followed by calcination at 800 °C for 6 h to get pure $LiMn_2O_4$ powders.

2.2. Synthesis of $LaPO_4$ coated $LiMn_2O_4$

$LaPO_4$ coated $LiMn_2O_4$ cathode materials were synthesized by polymeric process at the calculation of 1.0, 2.0 and 3.0 wt% of lanthanum nitrate hexa hydrate and phosphoric acid as the raw materials for coating. 2 g of the $LiMn_2O_4$ powder was dispersed in double distilled water with 3 h stirring. $LaPO_4$ coating calculated at 1.0, 2.0 and 3.0 wt% by using lanthanum nitrate hexa hydrate and phosphoric acid along with 5 ml of polyvinyl alcohol was mixed in warm distilled water and added drop wise to the dispersed $LiMn_2O_4$ solution. The mixture was stirred well for 5 h at room temperature. The resultant solution was evaporated at 60 °C for 10 h until a transparent sol was obtained. To remove water, the sol was heated at 60 °C while being stirred well. As the evaporation of water proceeded, the sol was turned into a viscous transparent gel. Thus the obtained gel precursor was dried in an air oven at 110 °C for 12 h to form a fine powder. It was calcined at 800 °C for 6 h to form a thin layer of $LaPO_4$ coated $LiMn_2O_4$ in the weight ratios of 99:1, 98:2 and 97:3.

2.3. Physical characterizations

Structural analysis was carried out by using a powder X-ray diffraction (Siemens D-5000, Mac Science MXP 18) equipped with a nickel filtered Cu-Kα radiation sources ($\lambda = 1.5405$ Å). The diffraction patterns were recorded between scattering angles of 15° and 80° at a step of 0.1°/min. The surface morphology of the coated materials was studied by using scanning electron microscopy (Hitachi model S-35000 V). The X-ray photon spectra of La 3*d*, P 2*p* and Mn 2*p* were recorded by XPS with monochromatic Al Kα radiation at 1450 eV. The spectrum was scanned in the range from 0.01 eV to 1400 eV with binding energy in 1 eV steps.

2.4. Electrochemical characterizations

The cathode materials were prepared by a doctor blade coating method with a slurry of 85 wt% of coated active materials, 10 wt% of conductive acetylene black and 5 wt% of polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidone (NMP) solvent. This mixture was then applied onto an etched aluminum foil current collector and dried at 110 °C for 12 h in a vacuum oven. The coated cathode foil was pressed and then cut into circular discs of 16 mm diameter. The button cells were assembled using stainless steel 2032 coin type containers in an argon filled glove box in which oxygen and water content were maintained below 2 ppm. Lithium foils were used as the anode and reference electrode. 1-M $LiPF_6$ with 1:1 ratio of ethylene carbonate and dimethyl carbonate (EC/DMC) was used as the electrolyte and a thin polypropylene film acted as the separator. The charge–discharge cycles for the assembled cells were performed by using a WPG100 Potentiostate/Galvanostate cycle life tester at a current density of 0.15 mA/g in the range between 4.5 and 3.0 V. The cyclic voltammogram (CV) experiments were carried out at a scan rate 0.1 mV/S between 3.0 and 4.5 V by using Auto lab modular electrochemical instruments (BST 7249).

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns for both the uncoated and $LaPO_4$ coated (1.0, 2.0 and 3.0 wt%) $LiMn_2O_4$ powders. All the powders showed well defined spinel structure with a space group of Fd3m, in which the lithium ions occupy the tetrahedral 8*a* site, whereas, Mn^{3+} and Mn^{4+} ions reside at the octahedral 16*d* site and O^{2-} ions located at the 32*e* site [25]. The XRD pattern of the obtained uncoated $LiMn_2O_4$ and

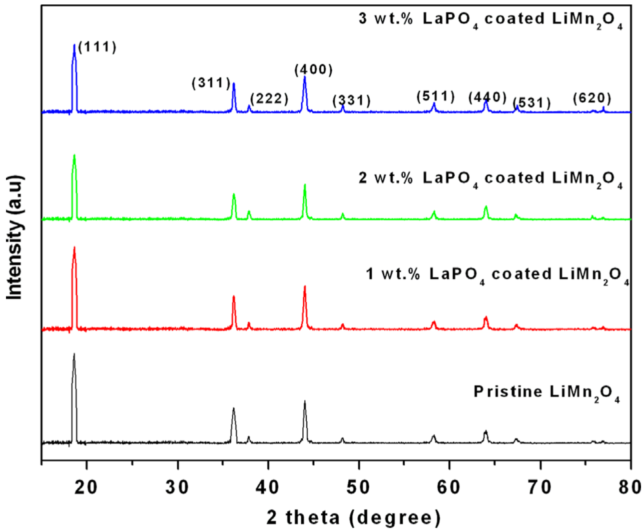

Fig. 1. X-ray diffraction patterns of uncoated and various wt% of $LaPO_4$ coated spinel $LiMn_2O_4$ powder materials synthesized at 800 °C.

$LaPO_4$ coated $LiMn_2O_4$ (1.0, 2.0 and 3.0 wt%) samples have matched that of a three dimensional structure listed in JCPDS data (# 89-0106). In addition, the $LaPO_4$ coating has not changed the 2θ value of the peaks. Moreover, the lattice constant of uncoated $LiMn_2O_4$, 1.0, 2.0, and 3.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ samples are 8.245, 8.246, 8.244 and 8.245 Å respectively. Earlier reports have showed that, substitution of transition metal ions form Mn^{3+} in $LiMn_2O_4$ with significant changes in lattice parameters [34,35]. In our case, significant changes in lattice parameters were not obtained. Based on these results, the presence of crystalline $LaPO_4$ was not detected by XRD. The bulk structure of $LiMn_2O_4$ remained unchanged after surface modification. No diffraction peaks belonging to $LaPO_4$ are detected for $LaPO_4$ coated $LiMn_2O_4$ powders. This indicates that, the surface coating layer was only a thin film and existed as an amorphous phase. These results revealed that, $LaPO_4$ is just coated on the surface of the $LiMn_2O_4$ powders. This phenomenon indicates that, the mechanism of coating is different from doping.

3.2. Surface morphology analysis

Fig. 2a and b show the SEM images of uncoated and 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ respectively. The surface morphology of the particles was distinctly changed upon coating. The brightness of the surface was increased in the coated samples compared to the pristine sample. It is associated with the accumulation of charge on the $LaPO_4$ coating materials as the electron beam impinges on it.

3.3. X-ray photon spectroscopy analysis

X-ray photoelectron spectroscopy has been widely used to study the electronic structure of the materials. The XPS binding energies has provided useful information on the oxidation state of different elements in materials. Fig. 3a shows XPS spectra of P 2*p* for 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ powder materials. The binding energy value of 134 eV corresponds to P–O [25]. Fig. 3b shows the binding energy value of Mn 2*p* XPS spectrum of $LaPO_4$ coated $LiMn_2O_4$. This spectrum displays that a broad emission line around 642.9 eV was combined with shoulder peak around 641.5 eV, which is assigned to Mn $2p_{3/2}$ spectra of Mn^{4+} and Mn^{3+} ions at octahedral sites in the spinel structure. Another peak was obtained around 653.9 eV which corresponds to Mn $2p_{1/2}$ spectra of Mn ions. In our experiments, the binding energy values are larger than 640.7 eV for Mn^{2+} in MnO [25]. This indicates that, the Mn valance state in $LaPO_4$ coated $LiMn_2O_4$ has a mixture of +3 and +4 oxidation states. We have observed the tallest peak at 531.8 eV from Fig. 3c, which corresponds to the binding energy value of O 1*s* in $LiMn_2O_4$; this may be assigned to the oxygen bonded to manganese ions. This binding energy value was in good agreement with previously reported value [24]. The XPS spectrum of La 3*d* in $LaPO_4$ coated $LiMn_2O_4$ is shown in Fig. 3d. The XPS spectrum of La 3*d* shows the characteristic peak at 836 eV similar to the binding energies of La in LaO_2 [26].

3.4. Galvanostatic charge/discharge studies

Fig. 4a and b show the typical charge–discharge curves of uncoated and $LaPO_4$ coated (1.0, 2.0 and 3.0 wt%) spinel $LiMn_2O_4$ cathode materials at a discharge rate of 0.5 C between the cell voltage 3.0 and 4.5 V at room temperature (30 °C) and elevated temperature (50 °C) respectively. At both the temperatures it can be seen that, $LiMn_2O_4$ samples with and without $LaPO_4$ coatings have similar charge–discharge profiles, exhibiting two charge–discharge plateaus in the potential region of 3.96 and 4.11 V which are ascribed to the remarkable characteristics of a well defined $LiMn_2O_4$ spinel and the voltage plateaus indicated that, the insertion and extraction of lithium ions occur in two stages [25]. The first voltage plateau at about 3.96 V is attributed to the removal of lithium ions from half of the tetrahedral sites in which Li–Li interaction occurs. The second voltage plateau observed at around 4.11 V is ascribed to the removal of lithium ions from the remaining tetrahedral sites. In the initial charge–discharge curves, the pristine $LiMn_2O_4$ samples have displayed slightly larger capacities than samples with $LaPO_4$ coatings. The inhomogeneous distribution of $LaPO_4$ coated $LiMn_2O_4$ materials would be ascribed to the lower initial capacity. The insulating $LaPO_4$ coated on the $LiMn_2O_4$ surface decreases the total conductivity of the materials and hinders the extraction/insertion of Li ions through the interface during the first cycle, which results in the poor initial discharge capacity of the cathode [36].

Fig. 5 shows the results of discharge cycling at 0.5-C rate between 3.0 and 4.5 V for uncoated $LiMn_2O_4$ and 1.0, 2.0 and 3.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ performed at 50 °C upto 100 cycles. The initial discharge capacity of $Li/LiPF_6/LiMn_2O_4$ is 125 mAh/g; it declines to 70 mAh/g after 100 cycles with a capacity loss of 44%. Such fast capacity fading is very common in $LiMn_2O_4$ [37,38]. This fast capacity fading was ascribed to the contribution of Mn^{3+} ions for Jahn–Teller distortion [39,40]

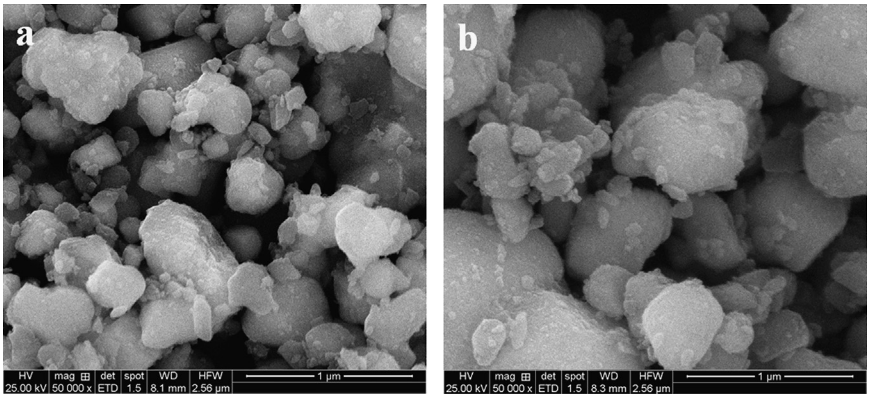

Fig. 2. SEM images of (a) uncoated and (b) 2.0 wt% of $LaPO_4$ coated spinel $LiMn_2O_4$ powder materials.

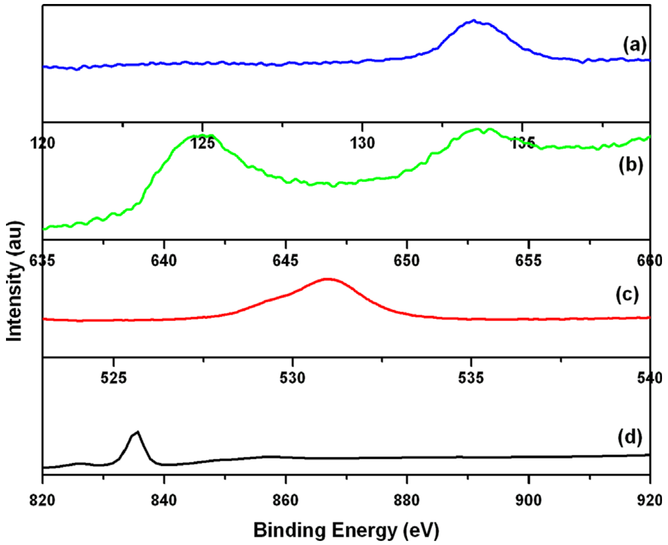

Fig. 3. XPS spectra of (a) P 2p, (b) Mn 2p, (c) O 1s, and (d) La 3d of a 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ powder materials.

during the cycling process at elevated temperature (50 °C). $LiMn_2O_4$ still suffers capacity fading at elevated temperature due to Mn^{3+} dissolution which resulted from side reactions, which occurred at the interface between an electrode and electrolyte during charge–discharge process.

The charge/discharge capacities of surface modified $LiMn_2O_4$ cathode materials have reduced a little with increasing coating content. This suggests that, even for the $LaPO_4$ coated spinel phase, only the Mn^{3+} contributes the charge–discharge capacities during the electrochemical reaction. The initial discharge capacities for 1.0, 2.0 and 3.0 wt% $LaPO_4$ coated $LiMn_2O_4$ are 109, 103 and 93 mAh/g respectively. $LaPO_4$ coated (1.0, 2.0 and 3.0 wt%) $LiMn_2O_4$ cathode materials have delivered the discharge capacities of 69, 82 and 71 mAh/g after 100 cycles respectively. 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ exhibits initial discharge capacity of 103 mAh/g, but after 100 cycles only 18% capacity loss was obtained and the discharge capacity is still maintained at 84 mAh/g. This cycling behavior of the $LaPO_4$ coated $LiMn_2O_4$ electrodes has indicated the impact of $LaPO_4$ coating significantly, which improved the electrochemical performances at elevated temperature. On the other hand, 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ shows the similar characteristics of two potential plateaus which were obtained at 3.96 and 4.11 V

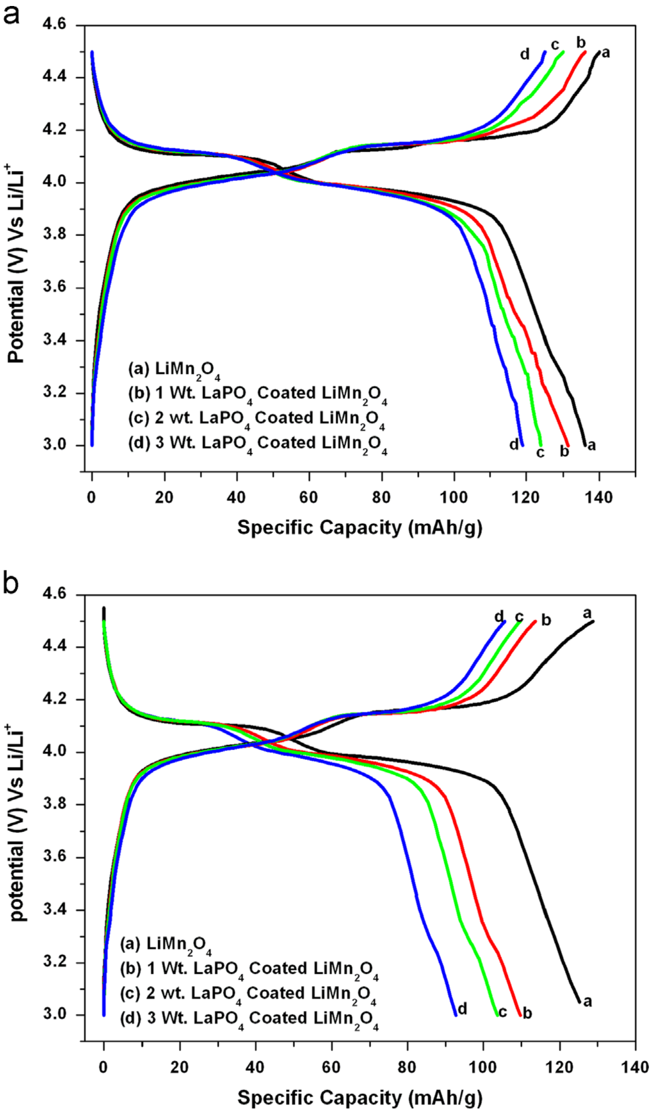

Fig. 4. Charge and discharge curves of pristine, 1.0 wt%, 2.0 wt% and 3.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ cathode materials between the range of 3.0–4.5 V at (a) room temperature (30 °C) and (b) elevated temperature (50 °C).

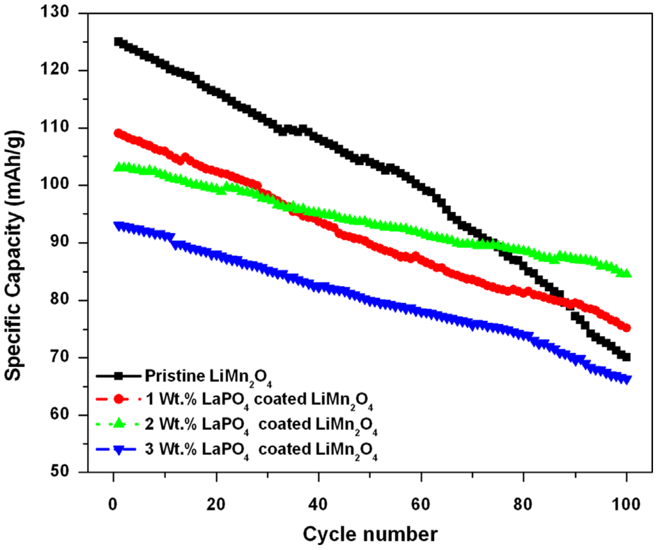

Fig. 5. Discharge capacities of uncoated $LiMn_2O_4$, 1.0 wt%, 2.0 wt% and 3.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ cathode materials between the range of 3.0–4.5 V discharge rate of 0.5-C at elevated temperature.

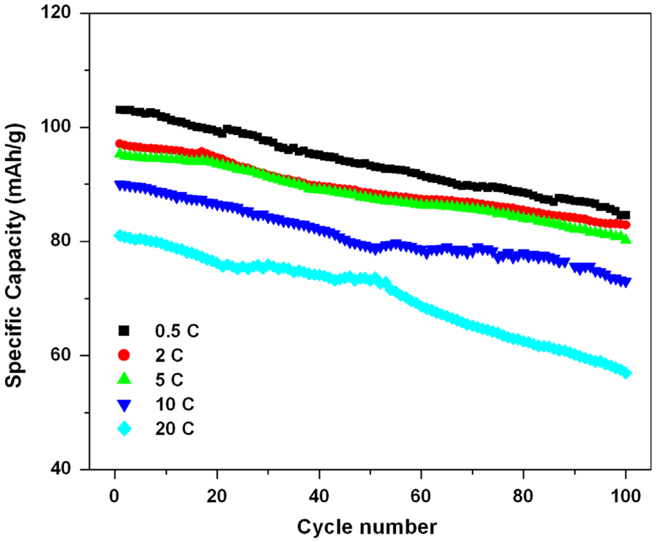

Fig. 6. Rate of discharge performance of 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ particles at elevated temperature.

compared with uncoated electrode. This indicates that, the $LaPO_4$ coating does not change the intrinsic property of $LiMn_2O_4$ during insertion and extraction of lithium ions. High and low percentages of $LaPO_4$ coated $LiMn_2O_4$ have lower capacity compared to optimum (2.0 wt%) coated concentration, because the addition of lanthanum nitrate content replaces the quantity of pristine $LiMn_2O_4$. Even in $LaPO_4$ coated $LiMn_2O_4$, Mn^{3+} only contributes the capacity during charge/discharge cycling. 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ is the optimum composition to enhance the stability and cycling performances of the electrode at elevated temperature. The $LaPO_4$ coated layers have been activated by Li ions transport and the movement of Li ion gradually opened the tunnel when the cycling increased. This result indicates that, the Li ion can easily penetrate the coated layer and deeply insert into the spinel. As a result, the discharge capacity has gradually reached the highest value after few cycles. This is in good agreement with the earlier result reported by Zheng et al. [36,39].

The 2.0 wt% $LaPO_4$ coating is actually the most effective in improving the cycling performance of $LiMn_2O_4$. Lower wt% $LaPO_4$ coated $LiMn_2O_4$ surface may not be protected efficiently and as $LaPO_4$ content increases from 2 wt% to 3 wt%, the cycling performance gets inferior. This manifests that, the $LaPO_4$ coating which can aid the diffusion of lithium ions for coating can facilitate the diffusion of lithium ions for the appropriate content. As $LaPO_4$ increases away from the optimum coating content, the excess insulating $LaPO_4$ will hinder the moving of lithium ions, leading to the evident decay of the capacity. This cycling behavior of the 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ electrodes has significantly improved the electrochemical performances at elevated temperature.

Fig. 6 shows the capacity retention of 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ cell at different discharge rates (charge at 1 C) characterized in the potential range between 3 and 4.5 V. The initial discharge capacities for 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ are 103 mAh/g at 0.5 C, 97 mAh/g at 1 C, 95 mAh/g at 5 C, 90 mAh/g at 10 C and 81 mAh/g at 20 C rates. The reversible capacity of the cell was gradually reduced in the first 20 cycles and then becomes stable. 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ cathode materials have delivered the discharge capacities of 84, 82, 80, 73 and 57 mAh/g after 100 cycles at a rate of 0.5 C, 1 C, 5 C, 10 C and 20 C respectively. Excellent capacity retention may be obtained at moderate rates. Based on the above results, 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ sample is an attractive material for practical applications. The good rechargeability and cycling stability of lanthanum phosphate coated $LiMn_2O_4$ were attributed to the fact that, Li^+ ion was re-inserted from spinel structure with a minimal contraction of the unit cell over a wide composition range.

3.5. Cyclic voltammetry studies

The typical cyclic voltammograms of uncoated $LiMn_2O_4$ and $LaPO_4$ coated $LiMn_2O_4$ electrodes were carried out by using pure lithium foil as the counter and reference electrodes, and 1-M $LiPF_6$ mixed with 1:1 ratio of ethylene carbonate and diethyl carbonate as the electrolyte in the potential range between 3.0 and 4.5 V at a scan rate of 0.1 mV s^{-1}. Fig. 7a and b show the initial and 100th cycles of the uncoated $LiMn_2O_4$ and 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ cyclic voltammetric curves at elevated temperature respectively. Cyclic voltammetric curves have shown the two symmetrical redox couples at around 3.96 and 4.11 V, which depicts the typical two stage intercalation/deintercalation of lithium ions respectively in the reversible spinel $LiMn_2O_4$ during the cycling process [27]. CV curves of pristine $LiMn_2O_4$ have two redox peaks couples around at 3.96 and 4.11 V vs Li/Li^+ (Fig. 7a). In the first cycle, two redox peaks are separated well and are narrow. After the 100th cycle, both anodic and cathodic peaks

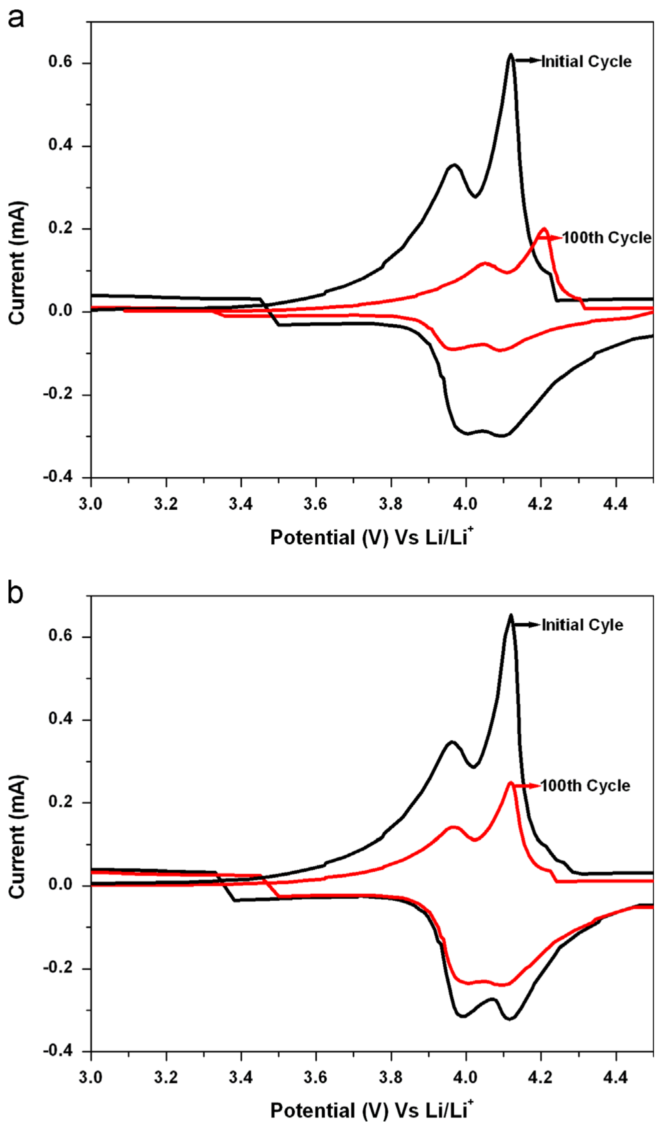

Fig. 7. Typical cyclic voltammogram curves of uncoated and 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ cycled at the potential range of 3.0–4.5 V at elevated temperature. (a) $LiMn_2O_4$ and (b) 2 Wt.% $LaPO_4$ Coated $LiMn_2O_4$.

are broader and closer to each other with smaller current peak intensities compared to the first cycle, which was ascribed to possible Jahn–Teller distortion. In Fig. 7a and b, both the oxidation and reduction peaks in the 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ cathode material are sharper than those of the pristine $LiMn_2O_4$ demonstrating a rapid electrode reaction after $LaPO_4$ coated sample. The intervals between the oxidation and reduction peak potentials of the optimum concentration of $LaPO_4$ coated $LiMn_2O_4$ are less than those of the pristine $LiMn_2O_4$, implying the decrease of polarization after $LaPO_4$ coatings. Furthermore, the oxidation and reduction peaks associated to 2.0 wt% $LaPO_4$ coated $LiMn_2O_4$ electrode are stable compared to the pristine electrode after 100 cycles. This result suggests that, $LaPO_4$ coating is very much useful to stabilize the structure of spinel $LiMn_2O_4$ during the electrochemical process at elevated temperature.

4. Conclusions

Spinel $LiMn_2O_4$ cathode materials were successfully coated with various wt% of $LaPO_4$ using lanthanum nitrate and phosphoric acid by polymeric process. XRD patterns for the $LaPO_4$ coated $LiMn_2O_4$ did not show any change in the 2θ value of the peaks, lattice parameters and no impurities were detected. The XPS results revealed that, the $LaPO_4$ was coated over the surface of the core $LiMn_2O_4$ powder materials. 2.0 wt% of $LaPO_4$ coated $LiMn_2O_4$ sample has significantly improved the capacity retention and excellent cycleability compared to the uncoated spinel $LiMn_2O_4$ and other surface modified cathode materials at elevated temperature. From these results it is believed that, the improved cycling performance of $LaPO_4$ coated $LiMn_2O_4$ is attributed to the ability of $LaPO_4$ layer in preventing direct contact of the active material with the electrolyte resulting in the decrease of electrolyte decomposition reactions and dissolution of active materials.

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