Lithium Titanate Films As High Performance Lithiumion Battery Anode

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Abstract:

We demonstrate the fabrication of porous lithium titanate (LTO) electrodes via facile electrophoretic deposition (EPD) technique. X ray diffraction pattern and scanning electron microscopy image of the deposited film revealed that as-deposited films were highly crystalline and porous in nature. Transmission electron microscopy confirms the primary particle size of around 30 nm while SEM image indicates clustered secondary particles of about 5 μm in size. Electrochemical evaluation of the LTO films delivered a stable capacity of 160 μAh/cm^2 at a current density of 0.10 mA/cm^2 while cycled at high current densities of 10 mA/cm^2, the electrode delivered a capacity of 130 μAh/cm^2 and stability for 1000 cycles. The excellent electrochemical performances of LTO film exposed the significance of EPD technique to develop high areal capacity electrodes for li-ion storage applications. High rate capability was enabled by the porous structure which permits electrolyte impregnation into the bulk of the electrodes maximizing electrode-electrolyte contact area.

Keywords: $Li_4Ti_5O_{12}$, anode, lithium ion battery, electrophoretic deposition, additive-free films

1. Introduction

Growing global energy need prompt researchers to focus on improving the power sources like battery technology to cater the portable energy market. Due to better potential features when compared to others Li-ion batteries have found wide application in the area of consumer electronics [1]. In recent years, considerable attention has been devoted for the fabrication of thin film anode material for Li-ion batteries [2]. Among anode materials, spinel lithium titanate ($Li_4Ti_5O_{12}$, LTO) is taking a leading role due to its potential features like zero stain volume, better structural stability, solving safety issues and improving battery life time. It provides a sufficiently high operating potential of 1.55 V against a lithium electrode with a theoretical capacity of 175 mAh/g, making it a highly safe anode materials for lithium ion batteries[3].

Thin film electrodes that are free from binders and conductive agents, provide high energy density and minimize cost. Hih performance of the battery also depend on the thickness, chemistry and stability of SEI layer formed [4]. Thinner electrodes in the form of films in a battery can improve high rate performance due to shorter ionic and electronic diffusion paths however, that limits the areal capacity [5]. Several techniques for LTO thin film fabrication have been reported [6-10], these techniques have known limitations including, high temperature for crystallization, low deposition rates, limited thickness and dense films without porosity leads to poorperformance.

In the present work, we report the fabrication of $Li_4Ti_5O_{12}$ films by EPD method using solvothermal synthesized nanoparticles. The crystallinity, morphology and electrochemical property of as-deposited film were investigated using X-ray diffraction, electron microscopy and galvanostatic charge-discharge tests. High areal capacity of 160 μAh/cm^2 was recorded at a current density of 0.10 mA/cm^2 while an areal capacity of 130 μAh/cm^2 was

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retained at 10 mA/cm^2 current density. At these high rates the LTO films also exhibited cycling stability over 1000 cycles with excellent capacity retention.

2. Experimental

2.1 Materials andmethods

LTO nanoparticles were synthesized using solvothermal technique as reported by Liu et. al. [11] and annealing condition was optimized as 500°C for 6 hr. EPD technique was adopted to optimize and fabricate LTO film on stainless steel substrate (SS 316). EPD of LTO nanoparticles was done by dispersing 50 mg LTO in 10 ml isopropyl alcohol. Upon obtaining a proper dispersion by sonication, the solution was transferred to a beaker immersing two stainless steel electrodes connected to a voltage source. Optimized EPD conditions of 40 V and 5 min, yielded LTO films of loading equivalent to 1.0 mg/cm^2. Subsequent to deposition, the films were dried in oven at 70°C prior to structural, morphological and electrochemical analysis. Structural analysis was carried out using x-ray diffraction (Rigaku ultimate-IV Japan). Scanning electron microscopy (SEM) for surface analysis was recorded using JSM 6490 LA (JEOL-Tokyo, Japan) at an operating voltage of 15 kV. Transmission electrons microscopy analysis was obtained using FEI TECNAI G^2 operating at a voltage of 200 kV. Fabricated LTO films were used as the working electrode and lithium foil as reference electrode for testing these films as Li-ion battery anode. The cell assembly was carried out in an argon filled glove box with H_2O and O_2 concentration maintained below 1 ppm. 1M $LiPF_6$ in EC/DMC was used as electrolyte. The cells were charged and discharged in the voltage window between 1.0 and 2.5 V at different current densities.

3. Results andDiscussions

3.1 Structural and morphologicalanalysis

X-Ray diffraction pattern of the EPD film (Fig. 1) confirms the phase purity of the cubic spinel LTO electrode. The peaks match well with cubic spinel LTO with space group of Fd3m. Intense (111) peak indicates good crystalline nature while broadness indicates the nanosized LTO particles.

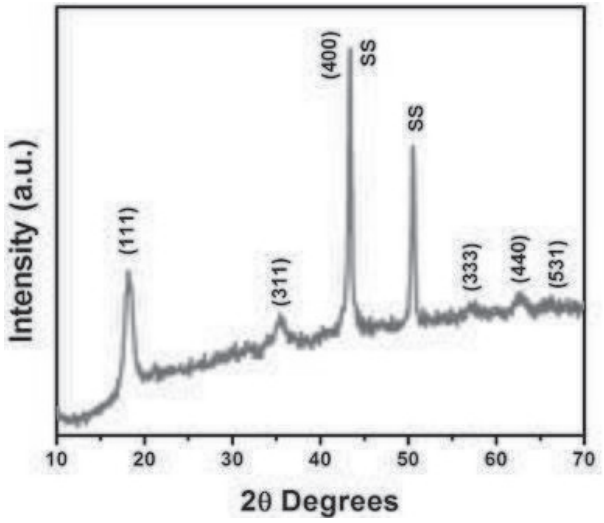


Figure 1: XRD pattern LTO film sample

Figure 2a shows low magnification (SEM) image of the electrophoretic deposited LTO films surface. Upon deposition the primary particles are clustered to form micron sized secondary particles and the film was observed to have proper adhesion to the SS foil possibly due to the addition of nickel nitrate. High magnification TEM image shows a crystalline LTO particle with an average particle size of 30 nm size (Fig. 2b).

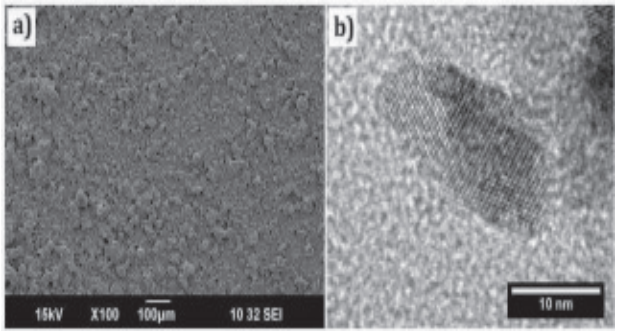


Figure 2: (a) SEM image of LTO film sample (b) TEM image of LTO nanoparticles

3.2 Electrochemical analysis

Fig. 3 shows the first three cycle's cyclic voltammetry curves of LTO films at a scan rate of 0.1 mV/s in the potential window ranging from 2.5 V to 1 V. Sharp peaks centred at 1.47 V and 1.64 V continuously overlap which confirm the excellent electrochemical reversibility of the deposited film. The sharp oxidation and reduction peaks indicate better kinetics of the film. The smaller insertion-de-insertion peak

separation shows the lower polarization effect [12, 13].

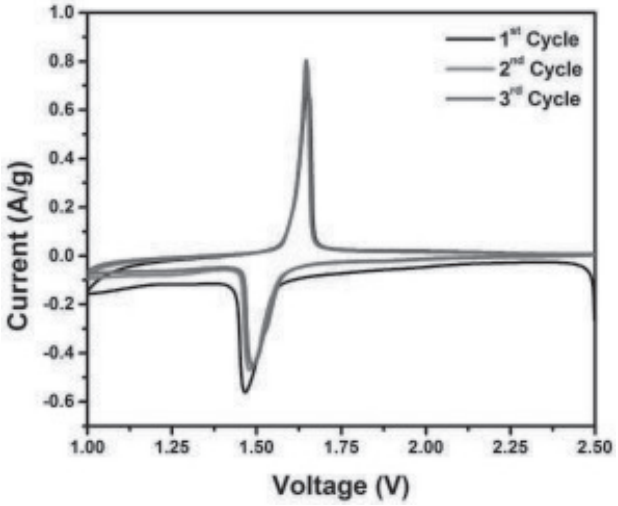


Figure 3: CV graph of LTO film

Fig. 4a shows the first cycle galvanostatic charge discharge curves of LTO films at different charge-discharge current densities ranging from 0.1 mA/cm^2 – 0.5 mA/cm^2 – 1.0 mA/cm^2 – 2.5 mA/cm^2 – 3.0 mA/cm^2. Except the 1st cycle all others have excellent reversibility with an areal capacity of 130 µAh/cm^2 even at high current of 3.0 mA/cm^2. Fig. 4b shows the rate performance of deposited films at different charge-discharge rates for a span of 5 cycles each. It shows excellent capacity retention, stability and Coulombic efficiency. Further to confirm the long cycling performance of LTO films, galvanostatic test were conducted at high currents of 10 mA/cm^2 (Fig. 4c). LTO electrode exhibited excellent cycling stability even at the end of 1000 cycle. Obtained areal capacitance value was 104.8 µAh/cm^2 with retention of 80%. This excellent performance of the EPD films were due to the formation of a porous film which lead to proper electrolyte percolation and rapid charge transfer[14].

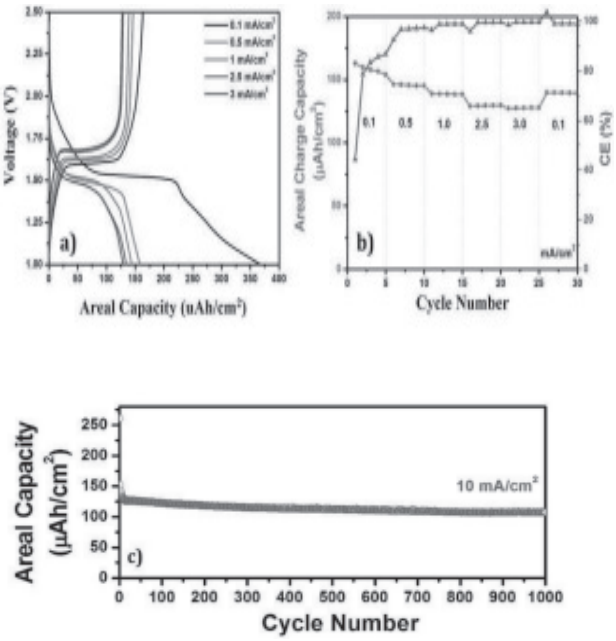


Figure 4: (a) charge-discharge profiles of LTO films at different rates indicated in legend (b) rate profile of LTO film (c) long cycling performance for 1000 cycles.

4. Conclusions

We have adopted solvothermal technique to synthesis LTO nanoparticles of average 30 nm in size. Further theses nanoparticles are successfully fabricated onto stainless steel substrate through electrophoretic deposition technique. Electrochemical performance of these LTO films as anode for Li-ion battery showed excellent electrochemical performances in terms of areal capacity and retention. An areal capacity of 160 µAh/cm^2 was delivered by the electrode at a current density of 0.10 mA/cm^2. At high current density of 10 mA/cm^2, LTO electrodes delivered a capacity of 104.8 µAh/cm^2 and retention of 80% for over 1000 cycles. These excellent performances of the EPD films were due to the formation of a porous film leading to proper electrolyte percolation and rapid charge transfer. Evolution of sharp oxidation and reduction peaks in cyclic voltammetry analysis further confirms the excellent reversibility and kinetics of LTO films. These results imply the promising potential of electro phoretically deposited LTO film electrode sand thuscan even beextended to flexible thin film battery applications. The first cycle irreversible capacity is an important aspect to be investigated and thus the present work provides scope for future studies for the same. The high rate capability and long cycling

stability indicates that these LTO electrodes could be used for li-ion capacitor applications which may also be studied in the future.

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6. References

1. P. Yang, P. Sun, and W. Mai, Mater. Today, 2016.19,394–402.
2. J. Li, C. Daniel, and D. Wood, J. Power Sources, 2011.196,2452–2460.
3. C. P. Sandhya, B. John, and C. Gouri, Ionics, vol. 20, no. 5. pp. 601–620,2014.
4. X. Han, M. Ouyang, L. Lu, and J. Li, Energies, vol. 7, no. 8, pp. 4895–4909,2014.
5. N. J. Dudney and B. J. Neudecker, Curr. Opin. Solid State Mater. Sci., 1999. 4, 479– 482.
6. C. L. Wang, Y. C. Liao, F. C. Hsu, N. H. Tai, and M. K. Wu, J. Electrochem. Soc., 2005. 152,A653–A657.
7. K. Tadanaga, A. Yamaguchi, A. Hayashi, M. Tatsumisago, J. Mosa and M. Aparicio, J. Asian Ceram. Soc., 2014.3,88-91.
8. R. Inada, K. Shibukawa, C. Masada, Y. Nakanishi, and Y. Sakurai, J. Power Sources, vol. 253, pp. 181–186,2014.
9. J. Mosa et al., J. Power Sources, vol. 244, pp. 482–487,2013.
10. Y. Zhao, G. Liu, L. Liu, and Z. Jiang, J. Solid State Electrochem., 2009.13,705–711.
11. G. Y. Liu, H.Y. Wang, G. Q. Liu, Z. Z. Yang, B. Jin and Q. C. Jiang, Electrochim. Acta, 2013. 87,218-223.
12. F. Wu, X. Li, Z. Wang and H. Guo, Nanoscale 2013.5,6936-6943.
13. Gao, L.; Li, S.; Huang, D.; Shen, Y.; Wang, M. J. Mater. Chem. A, 2015. 3, 10107-10113.
14. Chen, S.; Xin, Y.; Zhou, Y.; Ma, Y.; Zhou, H.; Qi, L. Energy Environ. Sci., 2014. 7, 1924-1930.