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Numerical modelling of transport limitations in lithium titanate anodes

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ABSTRACT

Lithium titanate oxide ($Li_4Ti_5O_{12}$, LTO) is receiving significant attention as an alternative to graphitic anode due to high structural and thermal stability, and reduced possibility of formation of SEI film. In this study, $Li_4Ti_5O_{12}$ is synthesized by the solid-state method and its electrochemical characteristics are examined by cyclic voltammetry and galvanostatic charge-discharge techniques. Moreover, we demonstrate the first instance of a numerical model used to understand the role of cell parameters in Li-LTO half-cells. The simulated charge-discharge capacity curves at 0.5, 1.0 and 1.5 C currents are in good agreement with experimental findings. Using this model, the effect of particle size, lithium diffusivity and electrode thickness on the charge-discharge capacity of Li-LTO cells have been investigated. Simulations show that the cell capacity is highly dependent on lithium transport in the solid matrix specifically at high current. Critical analysis of lithium concentration inside the solid matrix reveals a poor utilization of lithium storage sites and lower cyclable lithium in case larger particles and lower lithium diffusivity. The rise in the thickness of electrode leads to the lower achievable specific capacity of the battery due to increased cell overpotential and transport limitations for Li-ions and electrons.

1. Introduction

The enormous increase in energy demand, depletion of fossil fuel resources, increased global warming and environmental pollution due to the emission of harmful gases have drawn researchers towards alternative energy sources. Electric vehicles (EVs) and hybrid electric vehicles (HEVs) are being considered as a substitute for gasoline-powered vehicles which can reduce the dependency on fossil fuels and hazardous tailpipe emissions. Due to their highest gravimetric and volumetric energy densities, Li-ion batteries (LIBs) are receiving significant consideration to power these vehicles than other rechargeable battery systems [1,2]. However, the operation of LIBs at high current densities increases the rate of capacity loss by a rapid rise in rate-associated side reactions, such as electrolyte decomposition, active material dissolution, solid-electrolyte interface (SEI) film formation and gas generation [3–5]. Further, the high cost of materials used in the fabrication of LIBs makes these batteries expensive to fabricate. Several studies have been carried out towards the development of novel cathode [1,2,6] and anode [7–9] materials in order to enhance the electrochemical performance and discharge capacity of the LIBs. Carbon and its allotropes such as mesocarbon microbead (MCMB), artificial and natural graphite have been used as a commercial anode material due to their low redox potential (0.15–0.25 V) vs. lithium (Li/Li^+), good electronic conductivity (10^{-3} S cm^{-1}) and high Li-ion diffusivity (10^{-8}-10^{-10} cm^2 s^{-1}) with great structural stability during lithium intercalation and de-intercalation [9–11]. However, SEI film formation due to electrolyte reduction at the negative electrode is one of the main factors which are responsible for the capacity degradation of carbon-based anodes [3,9,12,13].

To overcome the problem of SEI formation, lithium titanate oxide ($Li_4Ti_5O_{12}$, LTO) has emerged as an alternative due to its almost zero strain (high structural stability) during Li-ion insertion and de-insertion, high rate capability and thermal stability [14,15]. LTO has a spinel type structure with reversible Li-ion insertion/de-insertion mechanism at room temperature. The electrochemical reaction at LTO anode is given as follows [16]:

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Nomenclature

a_s	electrode specific interfacial area (m^{-1})
A	surface area (m^2)
c	concentration (mol/m^3)
C	specific capacity (Ah/g)
D	diffusion coefficient (m^2/s)
ΔE_s	potential difference between consecutive relaxations (V)
ΔE_t	potential difference incurred due to applied current (V)
F	Faraday's constant (C/mol)
$f_\pm$	mean molar activity coefficient
i	current (A/m^2)
i_e	ionic current (A/m^2)
J	current density (A/m^3)
k	rate constant for electrochemical reaction ($m^{2.5}/(mol^{0.5}.s)$)
L	electrode thickness (m)
m	loading of the electrode (g)
M	molecular weight (kg/mol)
n	number of electrons
n_m	moles of active material (mol)
r	particle radius (m)
R_u	universal gas constant (J/(mol K))
t	time (s)
t_0^+	cation transference number
T	temperature (K)
U	equilibrium potential (V)
α_a	anodic transfer coefficient
α_c	cathodic transfer coefficient
ε	volume fraction
η	overpotential (V)
κ	ionic conductivity of electrolyte (S/m)
ν	molar volume (m^3/mol)
ρ	density (kg/m^3)
σ	solid-phase electronic conductivity (S/m)
τ	time of current pulse
φ	potential (V)

Subscript/Superscript

e	electrolyte
eff	effective
el	electrode
fl	filler
int	intercalation
ocp	open circuit potential
s	solid
0	initial

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \underset{Delithiation}{\overset{Lithiation}{\rightleftharpoons}} Li_7Ti_5O_{12} \tag{1}$$

Furthermore, LTO is a cheaper, non-toxic and easily produced anode and has Li/Li$^+$ potential plateaus at ~1.55 V [15–17] which can form 2V–class batteries with high voltage cathodes, i.e., $LiMn_2O_4$, $LiCoO_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [9–18]. The operating voltage of LTO is higher than the reduction potential of most electrolyte solvents which minimizes the possibility of formation of highly resistive SEI film at anode [19]. However, LTO has major drawbacks of lower electrical conductivity and lithium diffusivity, which results into increased polarization resistance in case of their use in high current applications involving LIBs [18–20].

To overcome the lower conductivity, coating of conducting materials over the surface of the LTO grains was demonstrated [20]. Others have also attempted to enhance the discharge capacity and capacity retention of LTO anode by reducing particle size which leads to decrease in diffusion length and increase in interfacial surface area for the electrochemical reaction [19–21]. Consequently, the nanostructured LTO powder can be considered as commercial anode material in LIBs in view of their high power applications in EVs and HEVs [9,22]. However, the detailed understanding of the effect of grain size, lithium diffusivity and electronic conductivity on cycling performance of LTO anodes have not been attempted so far. The quantification of the effect of these variables on cell performance through experimental measurements is difficult to achieve in practice. Therefore, numerical simulations using physics-based mathematical models are widely used as an alternative to carry out detailed parametric analysis, which can assist in quantifiable implications of cell variables on the charge-discharge capacity of LIBs. Moreover, such a modeling exercise for LTO electrodes is missing in the scientific domain. Hence, the objectives of the present study are as follows:

1. In-house measurement of cell parameters and development of an experimentally validated mathematical model for Li-LTO cells.
2. Using the developed model, conduct a parametric analysis of the Li-LTO cells for the identification of electrode particle size, lithium diffusivity and electrode thickness to maximize the charge-discharge capacity at different operational currents.

This study will reveal cell design features in order to improve the electrochemical performance of the LTO electrode for its possible use in high power and high energy density batteries.

2. Experimental method

2.1. Synthesis and characterization

The spinel-$Li_4Ti_5O_{12}$ powder was synthesized by the solid-state method using 8.69 g of TiO_2 (98%, Rankem) and 3.219 g of Li_2CO_3 (98%, Hi-Media) as titanium and lithium sources, respectively. The stoichiometric amount of the precursors was mixed and manually ground using agate mortar for 6 h. The ground mixture was calcined at 850 °C for 20 h, followed by the several hours grinding in order to obtain the pure phase of LTO powder. The crystal structure of the synthesized powder was analyzed by X-ray diffractometer (XRD: BRUKER D8 FOCUS) equipped with CuK$_\alpha$ radiation. The morphologies of the powder were analyzed by using FE-SEM (FESEM: MIRA3 TESCAN) and TEM (TEM: TECNAI G2 20 S-TWIN) techniques.

2.2. Fabrication and testing

The electrode slurry was prepared by mixing LTO (70%) with a binder (polyvinylidene fluoride (PVDF, 15%)) and conductive agent (super-P carbon black (15%)) and then dissolved in N-methyl 2-pyrrolidinone (NMP) solvent. The slurry was coated on a copper foil (thickness of ~15 μm) by doctor blade technique. Subsequently, the coated sheet was dried in air oven at 80 °C for 12 h to remove any traces of the solvent. After drying, the electrode sheet was pressed between stainless steel twin rollers to enhance the contact between