Journal of Power Sources 330 (2016) 84–91

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Rate limiting activity of charge transfer during lithiation from ionic liquids

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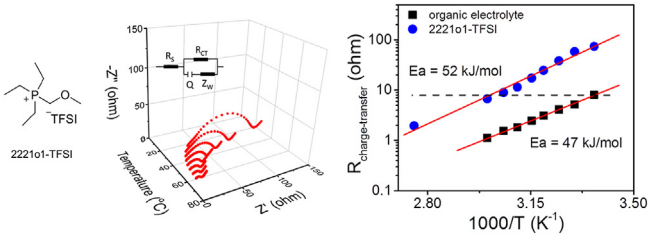
HIGHLIGHTS

- Charge transfer is the rate limiting step for lithiation in ionic liquids.
- Phosphonium cations facilitate the Li^+ desolvation in TFSI-based ionic liquids.
- High power performance is possible by reducing the charge transfer resistance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 July 2016
Received in revised form
23 August 2016
Accepted 28 August 2016

Keywords:
Ionic liquid
Li-ion battery
Kinetics
Activation energy
Electrolyte
Charge transfer

ABSTRACT

Given the increased use of room temperature ionic liquid electrolytes in Li-ion batteries, due to their non-flammability and negligible volatility, this study evaluates the lithiation kinetics to understand and improve the rate performance of Li-ion batteries. Lithium titanate spinel is used as a model electrode and the electrolyte is composed of LiTFSI and TFSI-coordinated alkoxy-modified phosphonium ionic liquid. Based on the analysis of activation energies for each process, we report that the charge-transfer reaction at the electrode/electrolyte interface is the rate-limiting step for cell operation. This finding is further supported by the observation that a 50-fold decrease in charge-transfer resistance at higher temperatures leads to a significant performance improvement over that of a traditional organic electrolyte at room temperature. Charge-transfer resistance and electrolyte wetting on the electrode surface are critical processes for optimal battery performance, and such processes need to be included when designing new ionic liquids in order to exceed the power density obtained with the use of current carbonate-based electrolytes.

1. Introduction

Li-ion batteries (LIBs) are a mainstay of modern society and used in large number of consumer products. As the demands for high performance LIBs increase as a consequence of additional applications in electric vehicles, surgical tools and other emerging industries, so do the requirements of increased energy densities, improved safety, reduced weight, faster re-charges, larger

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.119
0378-7753/

operating temperature ranges, and increased thermal stability. Many of the safety concerns associated with commercial Li-ion batteries arise from the use of organic solvents in the electrolyte, due to their volatility, flammability, and relatively low onset for thermal runaway [1–3]. Most of these limitations can be addressed by using room temperature ionic liquids (RTILs) as electrolyte solvents, given their thermal stability, non-flammability, and negligible vapor pressure [2,4–11]. Despite the promise, RTILs often exhibit lower ionic conductivities than conventional electrolytes, limiting their applicability for commercial use [12].

Significant research efforts are directed at tailoring ionic liquid compositions to exhibit higher ion mobilities and improved capacity retention at high cycling rates [13–17]. While the development of RTILs with low viscosity leads to a decrease in cell resistance and minimization of the ohmic drop during cycling, additional factors are likely to play a critical and capacity limiting role. In fact, lithium insertion into the electrode is a multi-step process [13,18,19], which includes the: i) migration/diffusion of Li^+ with its solvation layer in the electrolyte bulk; ii) desolvation of Li^+ and transfer through the double layer (charge transfer) at the electrode/electrolyte interface; iii) solid-state diffusion of lithium ions within the active material's particles; and iv) electron transport at the current collector/electrode interface. The last step is often thought to occur quickly, given proper distribution of conductive fillers in the electrode and a good contact with the current collector, and, thus, does not limit reaction kinetics. Consideration of the first three steps is necessary for a comprehensive analysis of the overall process.

In the present work, each of these steps is investigated during the lithium insertion and extraction processes using lithium titanate spinel ($Li_4Ti_5O_{12}$, LTO) as a model electrode, in a half-cell configuration, with an alkoxy-modified phosphonium ionic liquid electrolyte. The relative contributions of ionic conductivity, charge transfer, and Li^+ diffusion in the LTO lattice to the overall kinetics of the cell are evaluated, and the results provide insights into the essential features required for optimal battery performance.

2. Experimental

The ionic liquid (methoxymethyl)triethylphosphonium bis(trifluoromethylsulfonyl)imide (2221o1-TFSI) was prepared by mixing triethylphosphine (33.0 mmol, 3.90 g) and bromomethyl methyl ether (36.3 mmol, 4.54 g) in the glove box under argon atmosphere, and then sealed with a rubber septum and removed from the glove box. The mixture was refluxed under nitrogen at 78 °C in 25 mL of THF. A white solid was obtained and the reaction was completed after 24 h to yield (methoxymethyl)triethylphosphonium bromide (2221o1-Br). The crude intermediate was subjected to high vacuum at 80 °C to remove any volatile components. Next, 2221o1-Br (32.9 mmol, 8.0 g) and LiTFSI (42.8 mmol, 11.32 g) were mixed in 50 mL of a binary solvent of DCM and DI H_2O (1:1 v/v) with vigorous stirring at 40 °C for 12 h to yield the product 2221o1-TFSI. The product was washed by 3 × 15 mL of water. The addition of 1 N $AgNO_3$ solution was used to confirm the complete elimination of bromide anion. The organic layer was dried on anhydrous $MgSO_4$ and the solvent was removed under reduced pressure and the product was dried under high vacuum at 80 °C with stirring overnight for further operation.

Ionic conductivity was performed using a Conductivity Meter (K912, Consort) that has a 4-electrode cell to prevent the polarization error and fouling of the electrode. The ionic liquid electrolytes were dried at 100 °C under high-vacuum overnight to remove any trace amount of moisture before testing. Samples were maintained in glove box filled with Ar during the measurement. A heating block was used to control the temperature and stirring was maintained during the measurement to maintain homogeneity. A 30-min equilibration time was used at each temperature.

Viscosity was measured with an AR 1000 Controlled Strain Rheometer from TA Instruments equipped with a Peltier temperature control using a 20 mm diameter parallel aluminum plate. The gap was set to be 1.0–2.0 mm in all the runs. To minimize the effect of moisture in the air, the experiments were performed in a glove bag filled with nitrogen gas. Prior to each test, a pre-shear was done at shear rate 100 1/s for 10 s to eliminate the physical memory of the sample, followed by a 15-min equilibrium step in order for the sample to reach a steady state condition. Strain amplitude from 0.1 to 10% was determined to lie within the linear viscoelastic region (LVR) via an oscillatory strain sweep at a fixed frequency (1 Hz). Oscillatory temperature sweep was conducted from 10 °C to 95 °C with increment of 20 °C and 3-min equilibrium at each temperature. Strain and frequency were set to be 0.1% and 1 Hz, respectively. The Walden plot was constructed by association of experimental viscosity values and molar conductivities. The latter was calculated by dividing experimentally determined ionic conductivities by density values approximated by the methods described in Refs. [20,21].

LTO (Lithium Titanate, LTO, <200 nm particle size, spinel, Sigma-Aldrich) electrodes were prepared by casting the slurry with a coating machine (TQC), with a speed of 5 mm s^{-1} and a wet thickness of 60 μm. The slurry was prepared using N-methylpyrrolidinone (Sigma-Aldrich) as solvent and contained 80% active material (Sigma-Aldrich), 10% poly(vinylidene difluoride) binder (PVDF, Sigma-Aldrich) and 10% Super P carbon conductive filler (kindly provided by Imerys Graphite and Carbon). Active material loading was 2–3 mg/cm^2.

The ionic liquid-based electrolytes consisted of a 1 mol/L solution of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Sigma-Aldrich) in 2221o1-TFSI. A 1 mol/L solution of $LiPF_6$ solution in ethylene carbonate and dimethyl carbonate (EC:DMC 1:1 v/v, Solvionic) was also employed as a benchmark conventional electrolyte.

Electrochemical testing was performed using 2032-type cells in a half-cell configuration with a quartz membrane (Whatman) as a separator. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with an Autolab PGSTAT 302 N potentiostat. The CVs were obtained at different scan rates and the EIS was performed at open-circuit potential, with 5 mV amplitude in the range of 100 kHz − 100 mHz. To guarantee that all cells were at the same state of charge at different temperatures, EIS experiments were performed in LTO half-cells that have been previously fully lithiated at C/10 at room temperature. Charge-transfer resistances were fitted assuming a single time constant, in agreement with the absence of significant contribution from a permanent SEI-like layer in LTO electrodes [8,13,22,23]. Galvanostatic cycling was performed on a LAND CT2001A battery tester (cells at 24 °C) and on an Arbin Instruments BT-2000 battery cycler (cells at 90 °C), at the indicated rates.

3. Results and discussion

The 2221o1-TFSI phosphonium ionic liquid was chosen as the electrolyte based on the following considerations. First, phosphonium-based ionic liquids possess high chemical, electrochemical and thermal stability [5,6], along with enhanced lithium ion transport properties compared to other RTILs [24]. Although their ionic conductivities tend to be low when large side chains are present, the use of smaller cations results in reduced viscosity and higher conductivities [5]. Replacing a methylene of the alkyl chain of the ionic liquid with an ether linkage further reduces its viscosity and improves ion transport properties [6,24–26], and various