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Electrolytic solvent effects on the gassing behavior in LCO||LTO batteries

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ABSTRACT

$Li_4Ti_5O_{12}$ (LTO) is a promising anode material in both electrified vehicle and stationary energy storage applications for its superior rate capability and ultra-long cycle life. However, its widespread automotive utilization is hindered by electrolyte decomposition and gassing issues during high temperature (55 °C or higher) exposure. The exact mechanism of this gas generation is still not widely understood, and a specific commonly accepted solution for this issue has not yet been reported. In this study, $LiCoO_2$/$Li_4Ti_5O_{12}$ full cells are fabricated with three different electrolyte compositions and charged/discharged over different potential ranges (1.5–2.8 V, 1.5–2.9 V and 1.5–3.0 V) in room temperature or 60 °C. We find that the electrolyte component, in particular with respect to the cyclic carbonate content, exhibits significant influence on the gassing behavior; electron donating groups are helpful in gas suppression. Meanwhile, test temperature and up cut off voltage (UCOV) also influence the gassing behavior. For example, very limited gassing phenomenon is observed when the battery is tested at 60 °C or lower temperature with suitable electrolyte and UCOV below 2.9 V, while gas is produced when the UCOV is increased to 3.0 V or higher.

1. Introduction

$Li_4Ti_5O_{12}$ (LTO) is a zero strain material [1] with ultra-long cycle life. LTO-based lithium ion batteries (LIBs) have good cycle stability and excellent rate performance, as well as good abuse tolerance in overcharge or nail penetration [2–5]. For these reasons, LTO is considered as one of the important anode materials for both electrified vehicles (EV) and stationary energy storage (SES) batteries. However, LTO based LIBs suffer from serious gassing issues and capacity degradation when exposed to elevated temperatures, such as 55 °C or higher. Although several groups studied the gassing origin, no commonly held conclusion is evident in the literature yet. Wu [5,6] and Bernhard [7] et al. investigated the reaction between LTO and trace water in the battery, potentially producing H_2 and causing the gassing. While Amine [4], He [8] and Yu's [9] group believed that LTO catalyzed the reduction of electrolyte solvents, such as EC, the process through which gas was produced. Wu et al. [5] also found that gas generation was reduced to the lowest level by electrolyte optimization, such as adopting a PC + DMC (1:1) electrolyte, although no mechanism was elucidated in their work.

Three basic electrolyte formulations were designed and prepared to explore the origin and potential remedies for the gassing issue. These three formulations based on EC, PC and FEC respectively were implemented into $LiCoO_2$|| $Li_4Ti_5O_{12}$ pouch cells and their electrochemical performances were evaluated at different temperatures. It was found that the gassing issue is strongly but not solely dependent on electrolyte composition, in particular with respect to the cyclic carbonate content. Gassing could be effectively suppressed via electrolyte component and cut-off voltage optimization.

2. Experimental

2.1. Pouch cell fabrication

Pouch cells were fabricated with $LiCoO_2$ (LCO, supplied by Xiamen Tungsten Co., Ltd, China) as cathode and LTO (supplied by

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Xingneng Group, China) as anode. Both LCO and LTO electrodes were composed of active materials, polyvinylidene fluoride (PVDF, Solef 5130 by Solvay), and Super-P (Timcal, Switzerland) with a mass ratio of 90:5:5. The coating weight was controlled as 6.7 mg cm^{-2} for LCO and 5.0 mg cm^{-2} for LTO electrode, respectively. A cathode to anode capacity ratio of 1.1/1 was utilized for longer cycle life and better overcharge abuse response [10]. A PP membrane (Celgard 2325) was utilized as the separator. The cells were assembled by a typical pouch cell manufacturing process, and capacity of the cell was 40–45 mAh. Before electrolyte injection, the cells were further dried in a vacuum oven at 85 °C for 12 h to remove the residue moisture and avoid the influence of water.

2.2. *Design and preparation of the electrolytes*

Three cyclic carbonates were adopted in this paper, which is ethylene carbonate (EC, XinghwaChem, Dongying, China), propylene carbonate (PC, XinghwaChem, Dongying, China), and fluoroethylene carbonate (FEC, HSC Corporation, Zhangjiagang, China), respectively. They all have similar structure, and the only difference is the substituent group. The F in FEC is an electron withdrawing group; while the $-CH_3$ in PC is an electron donating group. A typical linear carbonate, dimethyl carbonate (DMC, XinghwaChem, Dongying, China) was adopted to reduce the viscosity and enhance the conductivity, and 1M $LiPF_6$ (Morita Chemical, Japan) was used and act as charge carrier, no additives were included to better understand the functions of each solvent. Three kinds of electrolytes were design and prepared based on the up mentioned principles, which are 1M $LiPF_6$/EC + DMC (4:6, wt) (abbreviated as ED), 1M $LiPF_6$/PC + DMC (4:6, wt) (PD), and 1M $LiPF_6$/FEC + PC + DMC (2:2:6, wt) (FPD), respectively. PC was added in the FEC based electrolyte to reduce the viscosity and improve the conductivity as FEC has a high viscosity of 4.1 mPa s as shown in Table 1 [11,12]. All electrolytes were prepared in a glove box filled with argon whose oxygen and hydrogen are both lower than 1 ppm. All the solvents were pretreated by molecular sieve to remove water and ensure moisture contents below 10 ppm (determined by a Mettler Toledo C20 Coulometric KF Titrator), on which to ensure residue moisture show little influence on the gassing phenomenon. Moreover, the mixture of electrolytic solvents must be cooled down to 0 °C before $LiPF_6$ was added to assure no overheat resulted decomposition would happen during the $LiPF_6$ addition process.

FEC is used in electrolytes for LIBs as it is believed to form an alternative solid electrolyte interphase (SEI) on both graphite [13] and silicon surfaces [14], and it also has a high oxidation potential (7.16 V *vs.* Li/Li$^+$), which makes it useful for cathode materials with

Table 1
Physical properties of solvents used in this paper.

Name	FW	ρ, g cm^{-3}	ε_r	η, mPa s	E_{homo}, eV	E_{lumo}, eV
Ethylene carbonate (EC)	88	1.32[a]	90[a]	1.9[a]	−12.86	1.51
Propylene carbonate (PC)	102	1.20	65	2.5	−12.72	1.52
4-Fluoro-1, 3-dioxolan-2one (FEC)	106	1.50	107	4.1	−13.30	1.45
Dimethyl carbonate (DMC)	90	1.06	3.1	0.59	−12.85	1.88

[a] Tested at 40 °C.

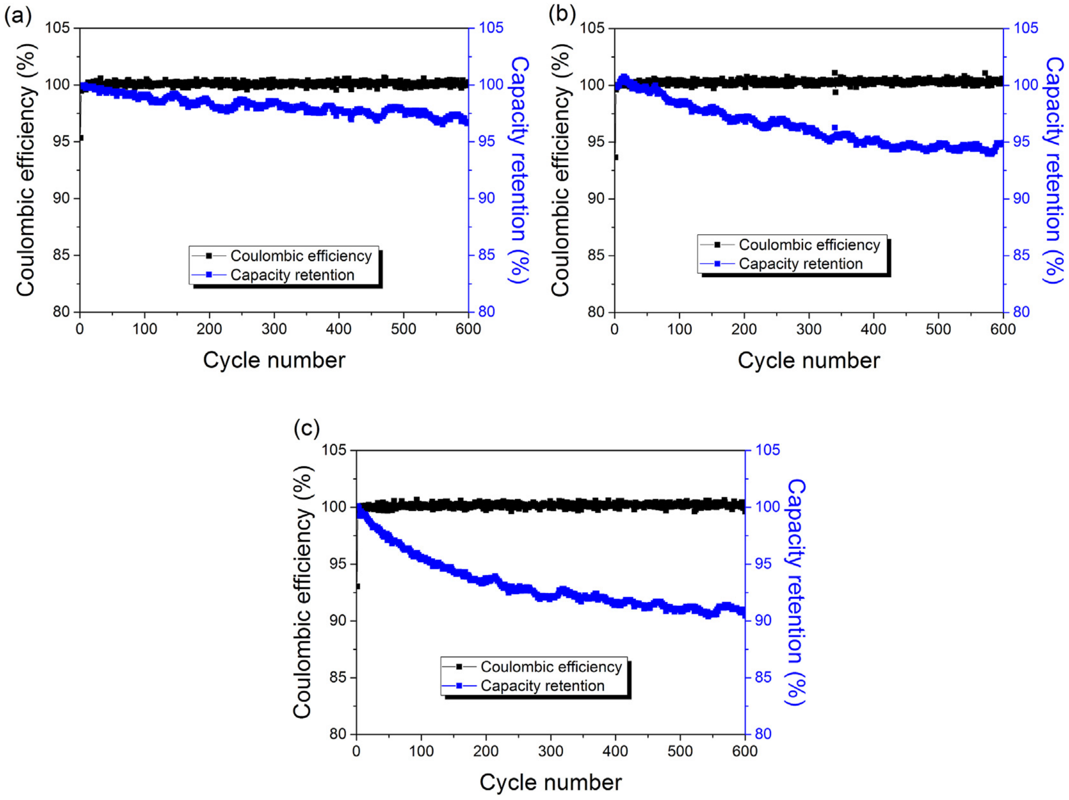

Fig. 1. Cycle performance of the $LiCoO_2/Li_4Ti_5O_{12}$ full cells (room temperature, 1C rate). (a) With ED electrolyte; (b) with PD electrolyte and (c) with FPD electrolyte.