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Temperature effects on $Li_4Ti_5O_{12}$ electrode/electrolyte interfaces at the first cycle: A X-ray Photoelectron Spectroscopy and Scanning Auger Microscopy study

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HIGHLIGHTS

- High temperatures promote the formation of a thicker SEI.
- XPS/SAM analysis along the first cycle evidence the SEI homogeneity.
- Temperature modifies the SEI chemical nature.
- Electrochemical performances vs temperature could be explained by the SEI features.

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ABSTRACT

$Li_4Ti_5O_{12}$-based negative electrodes for Lithium-ion batteries are of interest because of the high reversibility of Li^+ insertion/extraction. In this study, the surface of cycled electrodes is analysed by X-ray Photoelectron Spectroscopy (XPS) and Scanning Auger Microscopy (SAM) to investigate the effects of cycling temperature (room temperature, 60 °C and 85 °C) upon the solid electrolyte interphase (SEI) formation, which plays a major role in batteries electrochemical performances. Half-cells, with a vinylene carbonate containing electrolyte, are galvanostatically cycled at different steps of the first cycle: the mid-plateau during the first discharge, the end of the first discharge at 1.2 V and the end of the first charge at 2.0 V. XPS analysis evidences that higher temperatures promote the formation of a thicker SEI, which can explain the increase of the irreversible capacity with temperature. SAM mappings (allowing high spatial resolution ~10–100 nm) evidence that this SEI homogeneously covers the electrode surface, regardless of the cycling temperature. During charge, the SEI is partially dissolved at room temperature, more slightly at 60 °C whereas at 85 °C, no clear evidence of layer thinning is observed. The SEI chemical composition is also investigated and reveals a majority of organic species and an increasing proportion of LiF with the temperature.

1. Introduction

Nowadays, the need for efficient energy storage devices is constantly growing. Besides the high demand for portable electronic devices, load-levelling facilities needed for the integration of renewable energy sources in the global network and the intend of the automotive industry to democratize fully electrical vehicles, are increasing the expectations in terms of safety, capacity and reliability. Lithium-ion (Li-ion) batteries, due to their high versatility, can satisfy those requirements.

Spinel $Li_4Ti_5O_{12}$ (LTO) is considered as a good alternative negative electrode material for Li-ion batteries [1], due to its negligible change of lattice parameter during insertion/extraction of lithium ions [2], resulting in a very low capacity decrease upon cycling. This specificity compensates its low theoretical gravimetric capacity (175 $mAh.g^{-1}$) [3], compared to the one of graphite (372 $mAh.g^{-1}$), commonly used. Moreover, Li^+ insertion into/extraction from $Li_4Ti_5O_{12}$ occurs at a potential of around 1.55 V vs Li^+/Li^0, preventing any lithium plating.

The electrochemical stability of the electrolyte (which consists,

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in general, of a mixture of linear and cyclic organic carbonates and a lithium salt) toward the electrodes, is of prime importance in the maintenance of batteries performances [4]. Even if the potential of insertion/extraction of Li^+ ions is higher than the potential of reduction of a majority of organic solvents [5], the reactivity of LTO toward commons carbonates based electrolytes was firstly questioned by El Ouatani *et al.* [6]. Their X-ray Photoelectron Spectroscopy analysis revealed that during the first charge, carbonates salts (Li_2CO_3 and $ROCO_2Li$) and LiF were deposited on the surface of an LTO electrode cycled using $LiCoO_2$ as positive electrode material. An important gassing was also reported [7], inducing a swelling of LTO based batteries, which prevents their use on a large scale for security reasons. This gas release is supposed to occur at the electrode/electrolyte interface, therefore it is essential to better understand these interfacial phenomenons.

Consequently, the surface of LTO electrodes has been quite investigated, mainly in $Li_4Ti_5O_{12}$/Li half-cells in order to overcome possible interactions between negative and positive electrode: at low (<1.0 V) and high (>3.5 V) potentials [8] and between 1.0 V and 3.0 V [9]. In the latter, the authors explained that the electrodes are covered by a Solid Electrolyte Interphase (SEI). More recently, Nordh *et al.* [10] achieved a depth profile (using synchrotron tunable X-ray source) of the SEI formed after 5 and 200 cycles at room temperature, allowing to clarify its formation and chemical composition: mostly $LiP_xF_yO_z$, C—O and P—O containing species.

Some applications (for instance: electrical forklift or start & stop feature for cars) require both high rate (mainly for a quick charge) and high temperature capabilities [11,12]. The widely used graphite electrodes are known to undergo an important capacity fading at 80 °C due to the formation of a thick SEI [13]. On the contrary, it has been reported that LTO based electrodes are safer and more stable than carbon ones in a large range of temperature [14,15]. Moreover, high rate capability has been reported for those electrodes [16–20]. Therefore, the use of the LTO electrodes has been considered. However, an important gas generation has also been evidenced at higher cycling temperature [21–25]. Thus, Song et al. [26,27] studied the surface of carbon-free and carbon-containing LTO electrodes at room temperature and 60 °C. They evidenced the formation of a SEI upon cycling at room temperature and at 60 °C, accelerated by the presence of carbon at high temperature. While interfaces of carbon based electrodes have already been widely studied at high temperatures (60 °C [28], 65 °C [29], 80 °C [30], 85 °C [31], 120 °C [32]), only few works have been focused on LTO based electrodes operating in such conditions.

It has been shown that Vinylene Carbonate (VC) electrolyte additive promotes the formation of a passivating SEI on graphite electrodes, even at high temperatures [33–36]. Moreover, He et al. demonstrated recently that VC additive also contributes to a quicker protective layer formation on LTO electrodes, improving the rate and cycling performance of the batteries [9]. Therefore, we have decided to use the VC electrolyte additive in all our cycled batteries.

This work presents a systematic study of the effect of cycling temperature (room temperature, 60 °C and 85 °C) upon the interface layer formation at the LTO electrode surface. It is focused on the first charge-discharge cycle of a LTO/Li half-cell, with a VC-containing electrolyte. The samples were analysed by X-Ray Photoelectron Spectroscopy and Scanning Auger Microscopy, two complementary surface characterization techniques, operating at different spatial resolution. First of all, a precise analysis of the pristine electrode was performed. Then, the electrodes were analysed at various steps of the first cycle, at room temperature, 60 °C and 85 °C.

2. Experimental

2.1. Coin cells composition and assembly

The electrodes were provided by SAFT company. They were composed of a mixture of LTO (85% in weight), carbon black (CB) and carbon nano-tubes as carbonaceous additive ($10\%_w$) and poly(vinylidene fluoride) as a binder ($5\%_w$). The liquid electrolyte was a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight), containing $LiPF_6$ as lithium salt (1 $mol.L^{-1}$) and vinylene carbonate additive ($1\%_w$). A metallic lithium foil was used as a negative electrode. Coin cells were assembled in a glove box under argon atmosphere with low H_2O/O_2 level (<2 ppm).

2.2. Galvanostatic cycling

The obtained “half-cells” were then cycled at room temperature (RT), 60 °C and 85 °C under galvanostatic mode at C/10 rate (one Li^+ ion inserted per unit cell $Li_{4/3}Ti_{5/3}O_4$, every 10 h) from open circuit voltage with a Biologic MPG2 apparatus. Charge and discharge were stopped at several stages of the first cycle: at mid-plateau during the first discharge, at the end of the first discharge at 1.2 V and at the end of the first charge at 2.0 V. The high cycling temperatures were obtained by placing the coin cells in a thermostatic oven at 60 °C or 85 °C. Coin cells were then opened in a glove box (with low H_2O/O_2 level (<2 ppm)) and the LTO electrodes carefully separated from the rest of the cell components. The LTO electrodes were rinsed in a large excess of DMC in order to remove the remaining traces of electrolyte.

The electrochemical results obtained for the first charge-discharge cycle are presented for each temperature in Fig. 1. The curves obtained by galvanostatic cycling display a “plateau” of potential around 1.55 V for the three temperatures. This feature is characteristic of a two phases reaction occurring during discharge, involving a partially lithiated phase and a fully lithiated one. The number of electrons exchanged per unit formula ($Li_4Ti_5O_{12}$) at the end of the first discharge, increases with the temperature, ranging from 2.9 at RT to 3.3 at 60 °C and 3.7 at 85 °C. This indicates that more electrons are exchanged at higher temperatures to reach the same state of charge. Moreover, the irreversible capacity increases with the temperature at the first cycle: 13 $mAh.g^{-1}$ at RT, 35 $mAh.g^{-1}$ at 60 °C and 66 $mAh.g^{-1}$ at 85 °C (see Table 1).

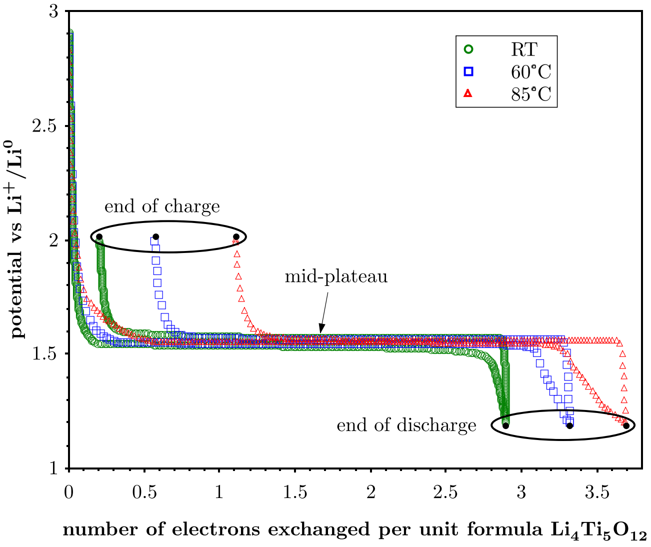

Fig. 1. Galvanostatic cycling (first cycle).