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Understanding the thermal instability of fluoroethylene carbonate in $LiPF_6$-based electrolytes for lithium ion batteries

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ABSTRACT

The cycling and storage performances of $LiCoO_2$ (LCO)-$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM)/pitch-coated silicon alloy-graphite (Si-C) full cells with ethylene carbonate (EC)–based and fluoroethylene carbonate (FEC)–based electrolytes are investigated at elevated temperatures. Excess FEC (used as a co-solvent in $LiPF_6$-based electrolytes), which is not completely consumed during the formation of the solid electrolyte interphase (SEI) layer on the electrodes, is prone to defluorination in the presence of Lewis acids such as PF_5; this reaction can generate unwanted HF and various acids (H_3OPF_6, HPO_2F_2, H_2PO_3F, H_3PO_4) at elevated temperatures. Our investigation reveals that the HF and acid compounds that are formed by FEC decomposition causes significant dissolution of transition metal ions (from the LCO-NCM cathode) into the electrolyte at elevated temperatures; as a result, the reversible capacity of the full cells reduces because of the deposition of the dissolved metal ions onto the anode. Moreover, we demonstrate possible mechanisms that account for the thermal instability of FEC in $LiPF_6$-based electrolytes at elevated temperatures using model experiments.

1. Introduction

Lithium ion batteries (LIBs) are perceived as suitable power sources for a variety of mobile electronic devices and a solution to the demand for ecofriendly electric vehicles and large-scale energy storage systems because of their high energy density and long cycle life. To improve the energy density of LIBs, electrode materials with high reversible capacities: cathode materials that operate at high voltages and anode materials with low working potentials close to 0 V vs. Li/Li^+ have been developed [1–3]. However, deterioration of the electrode–electrolyte interfaces causes unsatisfactory cycling performance of batteries. To stabilize the electrode–electrolyte interface, various approaches, such as surface-coating of the electrode materials and the use of electrolyte additives, have been proposed. Using reducible and oxidizable compounds for the formation of an artificial solid electrolyte interphase (SEI) is one of the most effective strategies to improve the interfacial stability of electrodes [4]. Si is considered a promising anode material for next-generation LIBs because of its high theoretical capacity of 4212 mAh g^{-1} for $Li_{22}Si_5$ [5]. Si anode materials cannot maintain their original structure because of the colossal volume changes that occur during cycling. Such large volume changes cause cracking of the Si particles to generate new active surface sites that may result in further irreversible electrolyte decomposition. Perpetual electrolyte decomposition at the Si anode depletes the electrolyte and degrades the anode. To improve the electrochemical performances of Si anodes, fluoroethylene carbonate (FEC) has been used as a highly effective reducible additive. It has been reported that FEC as an additive effectively modifies the nature of the SEI layer on the anode and improves the electrochemical performances of anodes such as graphite [6–8], and Si [9–16]. Previously, our group reported that Si thin-film/Li half cells with 3 wt.% FEC featured a substantially higher discharge capacity retention (88.5% after 80 cycles) than the FEC-free electrolyte (67.9% after 80 cycles) [11]. It should be noted that the optimum content of FEC as a promising reducible additive to improve the electrochemical performances of anodes in LIBs is dependent on the anode materials [6,9,12]. Despite the beneficial effects of FEC on the anodes, the decomposition mechanisms of FEC are still under investigation. FEC can decompose to vinylene carbonate (VC), which could produce the poly(VC) component of

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the SEI layer, and HF [6,17,21]. In addition to this reaction, polyacetylene and LiF can be produced as the SEI components by the electrochemical reduction of FEC on a Si electrode [13]. FEC can also be electrochemically reduced at the anode via opening of the five-membered ring leading to the formation of lithium poly(vinyl carbonate) ($(CH_2\text{-}CHOCO_2Li)_n$), LiF, and partially fluorinated dimers [15]. Gustafsson et al. demonstrated that the two most likely decomposition routes for FEC are defluorination and ring opening to form LiF and other organic species such as $-CHF\text{-}OCO_2$-type compounds [10]. However, there have been reports of detrimental effects of the FEC-derived SEI on the electrochemical properties of Li/graphite half cells and spinel-type $Li_{1.1}Mn_{1.9}O_4$/graphite full cells [18,19]. The capacity loss of the FEC-containing cell during storage at 60 °C was severe compared to those of VC-containing and additive-free cells. Recently, Lu et al. reported that the FEC additive did not prevent capacity fading of $LiMn_2O_4$ (LMO) cathode half cells at elevated temperatures [20]. They suggested that the HF formed via defluorination of FEC at elevated temperatures leads to increased Mn dissolution and the formation of a thick SEI layer on the LMO cathode.

Herein, we demonstrate the thermal instability of FEC as a co-solvent in high-energy-density lithium-ion batteries based on pitch-coated silicon alloy-graphite (Si-C) anode coupled with $LiCoO_2$ (LCO)-$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) cathode delivering high capacity of ~180 mAh g^{-1}. The differences in the surface chemistry of the Si-C anodes cycled in ethylene carbonate (EC)-based and FEC-based electrolyte are examined using ex situ X-ray photoelectron spectroscopy (XPS) measurements. The impact of FEC on the self-discharge of the Si-C anode in a full cell coupled with an LCO-NCM cathode during storage at 45 °C is discussed. Furthermore, we propose possible mechanisms that account for the thermal instability of the FEC solvent in presence of $LiPF_6$, leading to the inferior electrochemical performance of full cells at elevated temperatures.

2. Experimental

2.1. Preparation of the electrolyte and electrode

Two liquid electrolytes were tested: 1.5 M Lithium hexafluorophosphate ($LiPF_6$) in EC/diethyl carbonate (DEC) (3/7, w/w, EC-based electrolyte) and 1.5 M $LiPF_6$ in FEC/DEC (3/7, w/w, FEC-based electrolyte). All solvents and the $LiPF_6$ salt (Soulbrain Co., Ltd) were used as received. The water content of electrolytes was determined by Karl Fischer titration (C30, Mettler Toledo). The water content of EC-based electrolyte and FEC-based electrolyte was 12.5 and 10.0 ppm, respectively. To perform *ab initio* calculations of the reductive stability, optimized geometries of FEC and EC were obtained using Gaussian 09. Molecule optimization was carried out by applying density functional theory (DFT) with the B3LYP/6-311 + G basic set.

The anode was composed of 97 wt.% Si-C as the active material and 2 wt.% styrene-butadiene rubber/1 wt.% sodium carboxymethyl cellulose as the binder. Pitch-coated Si alloy (22.5 wt.%) was blended with 77.5 wt.% graphite to fabricate the Si-C anodes. The specific capacity and active material mass loading of the anode were 3.02 mAh cm^{-2} and 5.60 mg cm^{-2}, respectively. The cathode was composed of 97.8 wt.% LCO-NCM as the active material, 1.0 wt.% Super-P as the conducting agent, and 1.2 wt.% poly(vinylene fluoride) as the binder. The blend ratio of LCO and NCM in the cathode was 8/2, w/w. The specific capacity of the LCO-NCM cathode and loading of the active cathode material were 2.47 mAh cm^{-2} and 13.3 mg cm^{-2}, respectively.

2.2. Electrochemical measurements

LCO-NCM/Si-C full cells (2032 coin-type) were assembled with a microporous polyethylene film (SK Innovation Co., Ltd.) as a separator in an argon-filled glove box (O_2 and H_2O <0.1 ppm). Its thickness and porosity were 20 μm and 38%, respectively. LCO-NCM/Si-C full cells were galvanostatically precycled at a constant current of 9.25 mA g^{-1} (corresponding to C/20) between 2.5 and 4.2 V at 30 °C using a computer-controlled battery testing equipment (WonATech WBCS 3000). The constant voltage condition was applied to the end of the charge of precycling until the current was below C/100. Thereafter, the full cells were cycled at a constant current of 37 mA g^{-1} (corresponding to C/5) between 2.5 and 4.2 V at 30 °C for the standard cycle. The constant voltage condition was applied to the end of the charge of the standard cycle until the current was below C/50. After the standard cycle, the full cells were cycled at a constant current of 185 mA g^{-1} (corresponding to 1C) between 2.5 and 4.2 V at 60 °C. The constant voltage condition was applied to the end of the charge at every cycle until the current was below C/25.

To investigate the storage performance at an elevated temperature, the LCO-NCM/Li and Si-C/Li half cells and the LCO-NCM/Si-C full cells were stored for 20 days at 45 °C in a fully charged state, and then their capacity retention was measured at 30 °C. The capacity retention was calculated on the basis of the discharge capacity before storage.

2.3. Material characterization

After the 2nd cycle, the cells were carefully opened in a glove box to retrieve the Si-C anodes. The anodes were then rinsed in dimethyl carbonate to remove any residual $LiPF_6$-based electrolyte, and the resulting samples were dried at room temperature. These dried anodes were analyzed using ex situ X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher) with Al K_α ($h\nu$ = 1486.6 eV) radiation under ultrahigh vacuum with a 0.10 eV step and 50 eV pass energy. All XPS spectra were calibrated to the C—C bonding energy at 285 eV. To avoid any possible contamination, the samples for the ex situ XPS measurements were prepared in a glove box and sealed in an aluminum pouch under vacuum before use.

The surface morphologies of the Si-C anodes were determined by field emission scanning electron microscopy (FE-SEM, Nova NanoSEM, FEI), and energy dispersive spectrometry (EDS) was performed to identify the atomic composition of the surfaces of the Si-C anodes. All Si-C samples were retrieved from LCO-NCM/Si-C full cells that had been stored for 20 days at 45 °C with EC- or FEC-based electrolyte. The SEM and EDS samples were carefully prepared in a glove box to avoid any possible contamination. The samples were sealed in an aluminum pouch under vacuum prior to analysis.

To investigate the transition metal dissolution behavior of fully delithiated LCO-NCM cathodes in the EC- and FEC-based electrolytes, cathodes charged up to 4.3 V in the EC-based electrolyte were soaked in FEC solvent. The electrolytes, which were under argon in a polyethylene bottle that was sealed in an aluminum pouch, were stored in a convection oven at 60 °C for 24 h. The amounts of metal ions (i.e., Ni, Co, and Mn) in the electrolytes that had contact with the fully delithiated cathodes at 60 °C were measured via inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-II, Perkin Elmer). The amounts of metal ions deposited on the Si-C anodes retrieved from LCO-NCM/Si-C full cells that had been stored for 20 days at 45 °C were determined by means of ICP-MS.

To examine the thermal stability of FEC at an elevated temperature, typical experiments were performed. Solvent