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Degradation of surface film on $LiCoO_2$ electrode by hydrogen fluoride attack at moderately elevated temperature

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ABSTRACT

The failure mechanism of $LiCoO_2$ electrode at moderately elevated temperature (70 °C) is examined. To this end, a $Li/LiCoO_2$ cell is cycled 10 times within 3.0–4.3 V (*vs.* Li/Li^+) to deposit a surface film on the $LiCoO_2$ electrode, followed by storage at 70 °C for 10 h. The charge/discharge cycling data obtained at 25 °C after the storage reveal that the cell is damaged by the storage. The Coulombic efficiency decreases because the charging capacity is larger than that observed before the storage. The increased charging capacity is due to electrolyte oxidation. The postmortem analyses of the stored electrodes show that the surface film on the $LiCoO_2$ electrode becomes thinner after storage and with a notable compositional change compared to before storage. The increased charging capacity after the storage can be attributed to the extra electrolyte oxidation on the damaged (thinned) $LiCoO_2$ electrode surface. The loss of passivating ability due to surface film damage is responsible for the extra electrolyte oxidation and poorer Coulombic efficiency. Meanwhile, the chemical composition of the damaged film is very similar to that of the surface film stored with added hydrogen fluoride (HF, 400 ppm) in the electrolyte. It is thus suggested that the surface film is damaged by attack of HF generated from $LiPF_6$ during the high-temperature storage. Evidently, a decrease of $LiPF_6$ concentration in the electrolyte mitigates the film damage and the associated electrode degradation.

1. Introduction

Lithium-ion batteries (LIBs) are currently ubiquitous in electronic devices and electric vehicles for energy conversion and storage, due to their better performance than other candidates. Presently, the most popular cell components for LIBs are graphite for the negative electrode, lithium metal oxides of layered or spinel structure ($LiMO_2$, M = Co, Ni, or Mn; and LiM_2O_4, M = Ni or Mn) for the positive electrode, and $LiPF_6$-containing organic carbonate solvents as the electrolyte.

Frequently, LIBs are exposed to moderately elevated temperature (ca. 60–100 °C) through either heavy-duty use or abuse. Unfortunately, LIBs fabricated with these cell components can be degraded at this temperature, which shortens the cell life or triggers safety problems [1–4]. Hence, it is very important to unravel the failure mechanisms of LIBs in this temperature range and explore the appropriate countermeasures. Obviously, many components of the typical cells cannot be thermally degraded at 60–100 °C, such as the positive or negative active materials themselves, carbon conducting agent, and metal current collector [5]. Rather, the thermal generation of some reactive chemical species inside the cells and their attack on cell components are the more likely causes according to literature reports [6–11]. In particular, hydrogen fluoride (HF) as a reactive species should be considered, since it is easily generated via several routes. It is generated by the hydrolysis of $LiPF_6$ [12]. Above 60 °C, the thermal decomposition of $LiPF_6$ generates PF_5 [13,14], which further generates HF by reactions with either impurity water [15–17] or diethyl carbonate (DEC) of electrolyte [18–20]. Several undesirable effects from the as-generated HF have been reported [6–10]. For example, the $LiCoO_2$ (LCO) positive electrode can be attacked by HF to cause Co dissolution, and the dissolved metal ions are transferred to and plated on the negative electrode to cause self-discharge or cell degradation [6–8]. HF can also corrode the metal current collectors [9] and degrade the electrolytes [10,21].

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In the present LIBs, some amounts of electrolytes are inevitably reduced/oxidized at the negative/positive electrodes under the cell working conditions, leaving surface films on the electrode surfaces [22–27]. Fortunately, the surface films are electrically insulating, so that further electrolyte reduction/oxidation is prevented due to the passivating role of the surface films [22,23,27]. To achieve the best passivating ability, the surface films should be uniform, fully cover the electrode surface, and thicker than the electron tunneling length. When the surface film on the negative electrode is damaged to lose its passivation ability, electrolyte can decompose on the damaged areas and deposit new film to repair the damaged surface film. This process leads to capacity fading and eventually shortened cell life, and sometimes it triggers thermal runaway processes due to heat evolution [28–30]. Compared to the negative electrodes, the study of surface films on positive electrodes of LIBs (for example, LCO) is rather limited. Nevertheless, the generation mechanisms and the chemical compositions of the surface films on positive electrode have been reported [24,26,31–35]. The literatures illustrate that the surface films on positive electrodes are thinner than those on negative electrodes [24], but their chemical compositions are similar to those on negative electrodes. Given that these films contain both inorganic (LiF and Li_2CO_3) and organic (oligomers such as Li alkyl carbonates and polymers such as polycarbonate and polyethylene) species, it is very likely that the surface films on positive electrode are vulnerable to HF attack so as to the surface films on negative electrode [36,37].

Based on the context discussed above, this work attempts to answer the following questions: (i) whether the surface film on the LCO positive electrode is degraded upon exposure to moderately elevated temperature, (ii) if yes, whether the degradation is caused by the attack of reactive species such as HF, and (iii) how the film degradation affects the cell performances. To simulate the high-temperature exposure, a Li/LCO cell was fabricated and cycled to deposit surface films on the LCO surface, and then stored at moderately elevated temperatures (60 or 70 °C). After the storage, the cells were cycled again at 25 °C to check for signs of cell degradation. Postmortem analyses were performed on the damaged LCO electrodes.

2. Experimental

The composite electrodes were prepared from a slurry of LCO (KD10, Umicore), carbon conducting agent (Super P, Timcal), and polyvinylidene fluoride (PVdF, solef 6020, Solvay) (90:5:5 in wt. %) in *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich). The slurry was coated on Al foil with a doctor blade (loading amount: ca. 0.3 mA h cm^{-2}), and then pressed and dried at 120 °C in a vacuum overnight.

Two-electrode 2032-type coin-cells (Hoshen) were assembled with the as-prepared LCO composite electrode, separator (polypropylene/polyethylene/polypropylene, PP/PE/PP, Celgard), and Li metal. The electrolyte was 1.3 *M* $LiPF_6$ in ethylene carbonate (EC)/diethylene carbonate (DEC) (30:70 in vol. %, Panax etec).

After cell assembly, the first step was “pre-cycling”, i.e., galvanostatic charge/discharge cycling at 0.1 *C* (15 mA g^{-1}) at 25 °C for 10 cycles in the potential range of 3.0–4.3 V (*vs.* Li/Li^+) using a battery cycler (TOSCAT 3100, Toyo Co.). A rest period (10 min) was added between the cycles, and a constant voltage step was added in the charging period until the current decayed down to 0.01 *C* (1.5 mA g^{-1}). In the second step, the pre-cycled cells were stored at moderately elevated temperature (60 or 70 °C) for 10 h. Before the storage, the Li/LCO cell was discharged down to 3.0 V to adjust the state-of-charge (SOC) of LCO electrodes to zero and rested for 1 h. After storage, charge/discharge cycling at 25 °C (referred to as “re-cycling”) was performed at the same condition as for the pre-cycling, in order to examine possible cell failure due to the storage.

To confirm possible HF attack on the surface films, an HF contact experiment was also performed. To this end, the pre-cycled (surface-film deposited) LCO electrodes were immersed in EC/DEC (30:70 in vol. %) containing HF (400 ppm) and stored at the same condition (70 °C for 10 h). Note that $LiPF_6$ was not added to the solution in this experiment. To simulate possible PF_5 attack on the surface films, a flask containing $LiPF_6$ was heated at 70 °C to produce PF_5 gas, and the gas was transferred to another flask containing the pre-cycled LCO electrode heated at 70 °C (to simulate the storage at elevated temperature) [30].

The HF concentration in the electrolytes was measured by titrating with 0.01 *N* NaOH solution with an 888 Titrando titrator (Metrohm). The dissolved metal ion contents in the electrolyte solutions were analyzed by using inductively-coupled plasma mass spectrometry (ICP-MS, NexION 350D, Perkin-Elmer). For the measurement, the coin-cell was disassembled and all the cell components were washed with DEC to avoid the loss of electrolyte solution. The resulting DEC solution was used for the ICP sample. X-ray photoelectron spectroscopy (XPS, Sigmaprobe, UK) experiment was performed using Al Kα (1486.6 eV) radiation (15 kV, 10 mA) with a spot radius of ca. 200 μm. In an Ar-filled glove box, the sample electrodes were collected by disassembling the stored cells, washed with DEC, and dried under vacuum. For the washing, the electrodes were immersed in DEC for a few minutes and then gently shaken. The binding energy was calibrated with the C 1s peak (285.0 eV). The atomic concentration of any element *x* in the sample, C_x, was calculated using the following equation [38,39]:

$$C_x(\%) = \frac{I_x/S_x}{\sum I_i/S_i} \times 100$$

here, I_i is the number of photoelectrons per second detected from the analysis volume for atom species *i*, S_i is the atomic sensitivity factor, and I_x and S_x are the corresponding values for the element *x*. Fitting the XPS data and calculation of atomic concentrations were performed by Thermo Avantage software. Auger electron spectroscopy (AES, PHI700Xi, Physical Electronics) was conducted at 0° of tilt with an electron gun analyzer (10 keV, 10 nA) and a square-shaped spot 1–2 μm along the edge. The sample preparation and atomic ratio calculation were the same as those for the XPS measurements. Transmission electron microscopy (TEM, JEM-2100F, JEOL) analysis was performed at 200 kV. To prepare the sample, the composite electrode was carefully scraped from Al foil in an Ar-filled glove box. The obtained powder was dispersed in DEC by sonication, dropped onto lacey C-coated Cu grid, and dried under vacuum overnight.

3. Results and discussion

Fig. 1a shows the XPS spectra obtained from the fresh LCO composite electrode. The photoelectron peaks could be assigned to LCO (530 eV in O 1s and 780.6 eV in Co $2p_{3/2}$) [40] and PVdF binder (286.5 and 291.1 eV in C 1s, and 688 eV in F 1s) [41]. Photoelectrons emitted from Li_2CO_3 (290.0 eV in C 1s and 532 eV in O 1s) were also detected, which may be formed on LCO during the synthesis or storage in ambient atmosphere as a result of reaction with CO_2 [32,42]. LiF (685 eV in F 1s) was also detected, as the reaction product between LCO or Li_2CO_3 on the powder surface and hydrofluoric acid produced during the electrode fabrication process [32]. The XPS data in Fig. 1b reveal that the peaks of C-O (286.5 eV), C-O-C and C=O (287.8 eV), O=C-O (289.0 eV), and CO_3 (290.6 eV) in the C 1s spectra [39], and those of C=O and CO_3 (532 eV) and C-O (533.5 eV) in the O 1s spectra [32,43] became more intense after the