



Kinetic analysis of graphitized-carbon reactions in Li-ion cells before and after cycling degradation

Omar Samuel Mendoza-Hernandez^a, Eiji Hosono^b, Daisuke Asakura^b, Hirofumi Matsuda^b, Yoshitsugu Sone^{a,c}, Minoru Umeda^{d,*}

^a Japan Aerospace Exploration Agency, Institute of Space and Astronautical Science, 3-1-1 Yoshinodai, Chou-ku, Sagami-hara, Kanagawa 252-5210, Japan

^b Institute of Energy Conservation, National Institute of Advanced Industrial Science and Technology, (AIST) 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

^c The Graduate University of Advanced Studies, SOKENDAI, 3-1-1 Yoshinodai, Chou-ku, Sagami-hara, Kanagawa 252-5210, Japan

^d Nagaoka University of Technology, Department of Materials Science and Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

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ABSTRACT

The effect of cycling degradation on the kinetic characteristics of graphitized carbon electroactive material is investigated using laminated Li-ion cells incorporating a reference electrode. By carrying out electrochemical impedance spectroscopy (EIS) measurements at different state of charges and temperatures and obtaining dQ/dE vs. E curves, the pre-exponential factor and activation energy of Li-ion insertion/deinsertion reactions are analyzed as a function of anode potential. The kinetic behavior of charge transfer, Li-ion conduction and Li-ion solvation/desolvation reactions for Li-ion cells without degradation and after cycling degradation are investigated. Structural changes in the crystal structure of graphitized carbon originated from cycling degradation affect the charge transfer reactions, while irregular growing of the SEI affected the Li-ion conduction and Li-ion solvation/desolvation processes.

1. Introduction

Li-ion cells are an essential part of the power systems of electric vehicles, hybrid-electric vehicles and portable devices, and they have become the first choice to power aerospace applications, such as spacecraft and satellites. These applications demand a long lifetime, high performance and high safety level. However, there are still some concerns to achieve such demands, since many degradation processes have a direct impact on the performance and lifetime of Li-ion cells.

Li-ion cell degradation is caused by many physical and chemical processes, affecting different components of the cells [1–7]. Capacity fade is one of the main consequences of Li-ion cell degradation, this phenomenon is mainly caused by the electrolyte decomposition, solid electrolyte interface (SEI) growing and structural changes of electroactive materials [3–5]. Usually, the analyses of the degradation factors are made post-mortem, where the cells are disassembled after conducting degradation tests [4,5]. However, these analyses do not measure the reactions during degradation. Incremental capacity analysis is a good technique to evaluate Li-ion cells during degradation [7], but it is difficult to identify degradation factors taking place at a specific electroactive material when conventional Li-ion cells are used.

In-situ analysis of degraded Li-ion cells is very important to understand

how Li-ion insertion reactions are affected by different degradation processes. Electrochemical impedance spectroscopy (EIS) is an effective and nondestructive method to conduct in-situ analysis of the interfacial reactions in Li-ion cells, since it provides information on the electrochemical processes that take place inside the cell [8–12]. In our previous work, we studied the graphitized carbon based insertion/deinsertion reactions using a fresh (without degradation) Li-ion cell incorporating a reference electrode [13]. The combination of EIS measurements with Li-ion cells incorporating a reference electrode permits to independently analyze the anode and cathode electrode reactions. In this paper, we analyze and compare the Li-ion insertion/deinsertion reactions of graphitized carbon active material for non-degraded and cycling degraded Li-ion cells incorporating a reference electrode. EIS measurements and dQ/dE vs. E curves were used to analyze the effects of cycling degradation on the Li-ion insertion/deinsertion reactions of graphitized carbon.

2. Experimental

2.1. Li-ion cell specifications

Two laminated Li-ion cells incorporating a reference electrode were

* Corresponding author.

E-mail address: mumeda@vos.nagaokaut.ac.jp (M. Umeda).

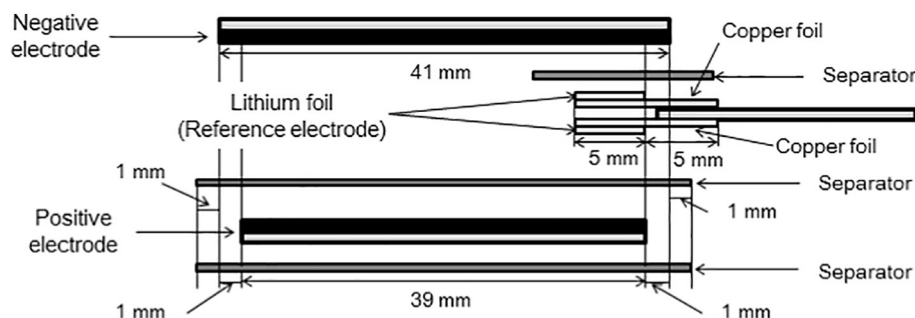


Fig. 1. Illustration of the laminated Li-ion cell incorporating a reference electrode. The cell uses LiCoO_2 and graphitized carbon as positive and negative electroactive materials. (Reprinted with permission from O. S. Mendoza-Hernandez et al., *Electrochimica Acta* 131 (2014) 168–173. License number 4193411213917 Elsevier Ltd.)

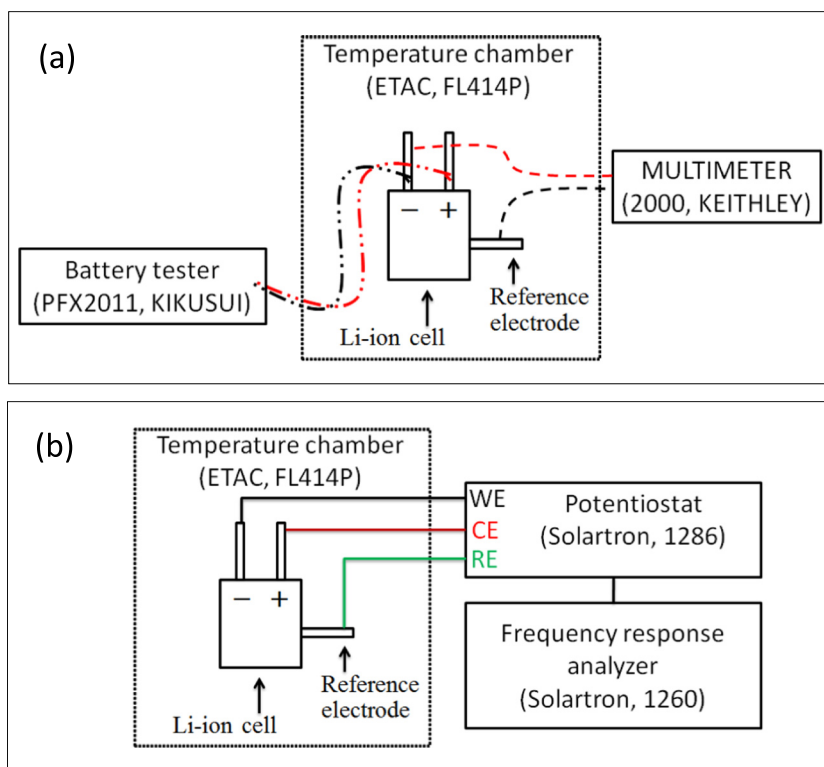


Fig. 2. Schematic setup of the Li-ion cells incorporating a reference electrode to obtain dQ/dE vs. E curves (a) and carry out electrochemical impedance spectroscopy measurements (b).

used in this work. Fig. 1 shows an illustration of the cell. The cells had LiCoO_2 as positive electroactive material and graphitized carbon as negative electroactive material. The nominal capacity was 20 mAh. Details about the Li-ion cell configuration, electrodes preparation and electrolyte composition are described in reference [13].

2.2. Cycling degradation test

One of the laminated cells was subjected to a charge-discharge degradation test at 35 °C. This temperature was chosen to accelerate the cycling degradation process. The cell was charged/discharged using a battery tester (KIKUSUI, PFX2011). During charge, a constant current-constant voltage (CC-CV) protocol was followed, where a constant current of 10 mA was applied until 4.2 V. The cell was discharged to 25% depth of discharge (DoD) following a constant current (CC) protocol with a discharging current of 10 mA. The total charge/discharge cycles were 94.

2.3. dQ/dE vs. E curves

The capacities of the fresh and cycling degraded Li-ion cells were

checked using a battery tester (KIKUSUI PFX2011). The cell was charged using a CC-CV protocol with a maximum voltage of 4.2 V and a CV time of 1 h 30 min. The cells were discharged using CC protocol until a cut-off voltage of 2.7 V.

Once the capacity C is obtained, the cell is subjected to constant current charge/discharge measurements. The conditions were set to a maximum voltage of 4.2 V during charge and a cut-off voltage of 2.7 V during discharge. A constant current of 0.2 °C was applied. During this process, the electrode potential of the negative electroactive material was recorded using a multimeter (KEITHLEY 2000), as illustrated in Fig. 2(a). Since the Li-ion cell capacity is a function of temperature, all the measurements were carried out at 25 °C to be able compare the dQ/dE vs. curves between the cells.

2.4. Electrochemical impedance spectroscopy measurements

To obtain the impedance spectrum of the negative electroactive material, a potentiostat (Solartron 1286) interconnected with a frequency response analyzer (Solartron 1260) was used, where the working electrode is connected to the anode, the counter electrode to the cathode and the potentiostat reference electrode to the reference

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