Proposal of simple and novel method of capacity fading analysis using pseudo-reference electrode in lithium ion cells: Application to solvent-free lithium ion polymer batteries

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HIGHLIGHTS

- Proposal of a simple pseudo-reference electrode for lithium ion battery.
- Separation of the cathode/anode potential and impedance using pseudo-reference.
- >1000 cycles operation using $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, solvent-free SPE, and graphite.
- Continuous lithium loss at the graphite is the main factor of the capacity fading.

GRAPHICAL ABSTRACT
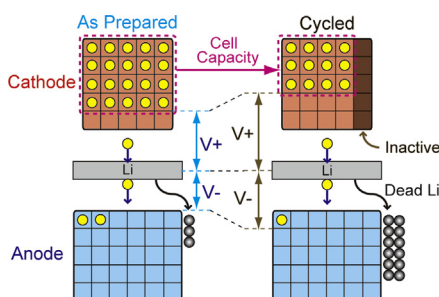
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ABSTRACT

We propose a simple procedure for introducing a pseudo-reference electrode (PRE) to lithium ion batteries using isometric lithium metal placed between the cathode and anode, and we successfully obtained the cathode and anode voltage profiles, individual interfacial impedances, and the misalignment of the operation range between the cathode and anode after cycle operation. The proposed procedure is applicable to lithium ion battery systems using a solid electrolyte to prepare two cells with a lithium counter electrode. We determined the capacity decrease of a solvent-free lithium ion polymer battery consisting of a $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), a polyether-based solid polymer electrolyte (SPE), and a graphite (Gr) with the proposed PRE over 1000 cycles. The capacity retention of the [Gr|SPE|NMC] cell reached 50% at the 1000th cycle upon the optimization of cell preparation, and we found that the main factor of the capacity decrease was the continuous irreversible loss of active lithium at the graphite anode, not the oxidation of the SPE. Our findings suggest that we should reconsider combining a polyether-based SPE with a conventionally used 4 V class cathode and a graphite anode to develop an innovative, safe, and low-cost battery for the expected large lithium ion battery systems for stationary use.

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1. Introduction

The application of lithium ion batteries has now begin to extend from mobile use to EV or stationary use. For such large systems, an operation life much longer than that of mobile systems is required. Thus, a complete understanding of the capacity fading mechanism of lithium ion batteries is important for the development of such long-life battery systems. Monitoring the voltage of the cell during charge and discharge is a basic approach to understanding electrode reactions inside the cell. However, as the anode materials in most lithium ion batteries have a potential slope, we cannot easily obtain the accurate potential of each electrode during operation.

The introduction of a reference electrode with a stable potential is a useful approach to monitoring the potential of each electrode in lithium ion cells [1–4]. However, the configuration of such cells designed to obtain a suitable reference electrode performance has not yet been optimized for the simple and long-term operation of the cells. One novel method of optimizing the configuration is to apply a lithium alloy material with a sufficiently fine (25 μm diameter) reference electrode [3]. Previous studies have successfully shown changes in the area specific impedance (ASI), the misalignment of electrode-capacity windows, and changes in the AC impedance during storage [5].

Our objective is to apply a solvent-free solid polymer electrolyte (SPE) in a lithium ion cell system [6,7]. The thickness of the SPE sheet used is 50 μm owing to its relatively low lithium ion conductivity. Therefore, we cannot use the so-called "beaker cell" because it requires a long electrolyte distance between electrodes. Furthermore, it is difficult to introduce the above-mentioned fine reference electrode into our system because of concerns regarding inhomogeneous current flow and the insufficient mechanical strength of the applied SPE. The distribution of current flow in the SPE requires stricter homogeneity than that in a liquid electrolyte because of the low lithium ion conductivity and immobility of the SPE.

With the above-mentioned restrictions, we propose a novel and simple lithium ion cell configuration, as shown in Fig. 1. Here, the anode is graphite (Gr) and the cathode is LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC). The anode and cathode are each encapsulated in a laminate pouch while facing isometric lithium metal, and each lithium electrode is externally connected outside the cells. This cell configuration can be described as [Gr|SPE|Li]–[Li|SPE|NMC], and an array of pair-type cells was named the "Nico-Ichi" -type cell. In the

configuration, we can use not only laminate pouch-type cells but also coin-type cells. In the configuration, the lithium metal acts as a lithium ion deposition/dissolution bridge and also as a pseudo-reference electrode (PRE) during charge and discharge. The proposed procedure of introducing the reference electrode may be in contrast to the procedure of formally introducing such an electrode. In addition, we cannot recommend using the proposed procedure if the dendrite growth of the lithium metal and the increase in impedance due to the introduction of the additional lithium and electrolyte interface significantly affect the cell performance. However, the proposed system has many merits as follows: (i) the cathode and anode voltage profiles and their interfacial impedances can be obtained, (ii) a homogeneous current distribution is guaranteed inside the cell because the reference electrode faces isometric cathode and anode materials, (iii) the capacity of each electrode can be quantitatively determined during or after operation by measuring the capacity of each half cell, and (iv) the misalignment of the operated state of charge (SOC) can be monitored and the anode or cathode SOC can be adjusted by supplying or absorbing lithium ions from the facing lithium metal reference electrode. Furthermore, (v) we can also use different types of electrolyte in each half cell at different temperatures to determine the degradation factor fpr the combination of an electrode and electrolyte. We applied the proposed lithium ion cells with a lithium PRE in a 4 V class [Gr|SPE|NMC] system and determined the capacity fading mechanism of the cell by analyzing cell voltage profiles, impedance trends, and the remaining electrode capacities after cycle operations.

2. Experimental

2.1. Polymer structure

We used a conventional polyether-based material (Fig. 2) as the SPE sheet [P(EO/MEEGE/AGE) = 82/18/2 (Daiso) where EO is ethylene oxide, MEEGE is 2-(2-methoxyethoxy)ethyl glycidyl ether, and AGE is allyl glycidyl ether] [8]. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 3 M) was added to the SPE at a molar ratio of [O]/[Li] = 16/1. The thickness of the SPE sheet used was approximately 50 μm. In addition, another SPE without an AGE bridging group, [P(EO/MEEGE) = 88/12 (MW = 1.5 M)], was used at the SPE and electrode interface by overcoating the SPE dissolved in acetonitrile (AN) on the electrode. Details of the overcoating procedure were reported previously [9]. The lithium salts used were LiTFSI at the Gr|SPE interface and lithium tetrafluoroborate (LiBF$_4$) at the NMC|SPE interface to prevent the corrosion of the aluminum current collector induced by LiTFSI. The apparent ionic conductivity, which was obtained from R_s (ACσ), exhibited an order (10^{-4} S cm^{-1} at 333 K) similar to that in a previous report [10].

2.2. Electrode preparation

90.4 wt.% NMC was mixed with 6.4 wt.% conductive additives (3.2 wt.% carbon black and 3.2 wt.% VGCF®, Showa Denko) and a 3.1 wt.% water-based binder (2.1 wt.% carboxymethylcellulose; CMC and 1.0 wt.% styrene butadiene rubber; SBR). The choice of the

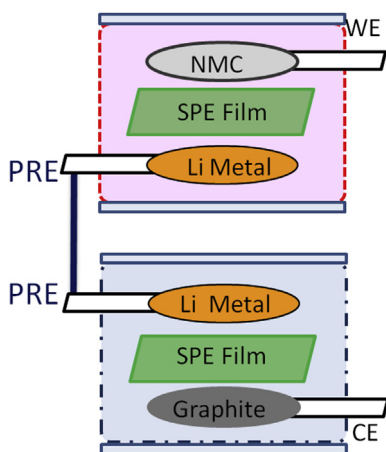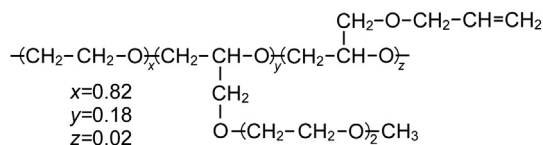**Fig. 1.** Schematic of proposed array of pair-type lithium ion cells with pseudo-reference electrode (PRE): Nico-Ichi-type cell.

Fig. 2. Structure unit of SPE used.