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Factor affecting the capacity retention of lithium-ion cells

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Abstract

Capacity failure due to the imbalance of coulombic efficiencies between positive and negative electrodes in a lithium-ion (shuttlecock) cell was examined by fabricating two types of cells, i.e., $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4/\text{LiNiO}_2$ and carbon/ LiNiO_2 . Rechargeable capacity of a lithium-ion cell consisting of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and LiNiO_2 faded more rapidly than that of a cell based on natural graphite and LiNiO_2 in spite of superior coulombic efficiency of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (very close to 100%) compared with that of natural graphite (about 98%). The important role of the electrolyte upon the capacity retention of lithium-ion cells is described and specific problems to extend cycle life are discussed.

Keywords: Lithium-ion cells; Capacity; Rechargeable lithium cells

1. Introduction

Lithium-ion (shuttlecock) cells have been of great interest among battery researchers since the implementation of this innovative secondary system [1]. Candidate materials examined for positive electrodes are LiCoO_2 [2], LiNiO_2 [3], $\text{LiCo}_{1/2}\text{Ni}_{1/2}\text{O}_2$ [4,5], LiMnO_2 [6,7], and LiMn_2O_4 [8,9]. Materials for negative electrodes are mostly carbon [10,11] in order to retain a high-voltage character while conventional cathode materials for rechargeable lithium cells can be used. Combination of these materials in an appropriate electrolyte gives a lithium-ion cell that does not contain any lithium, so that several lithium-ion cells having different operating voltages, and their profiles, can be made such as LiCoO_2 /non-graphitized carbon [1,12], or graphitized pitch-based carbon microbead [13], LiNiO_2 /petroleum coke [14] or natural graphite [15], LiMn_2O_4 /petroleum coke [16], $\text{LiCoO}_2/\text{TiS}_2$ [17,18], and so forth. However, little is known about the important role of electrolytes upon the capacity retention of lithium-ion cells. In this paper we report on the cycle behaviour of lithium-ion cells, $\text{LiNiO}_2/\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and LiNiO_2 /carbon (natural graphite), and discuss the important properties of the electrolyte for a lithium-ion cell to extend cycle life.

2. Experimental

LiCoO_2 , LiNiO_2 , and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ were prepared by the following methods. LiCoO_2 was prepared from

CoCO_3 and Li_2CO_3 . Known amounts of the raw materials were well mixed and pressed into pellets (23 mm diameter and about 5 mm thick). The pellets were heated in air at 650 °C for 12 h. The precalcined black mixture was then ground, pressed into pellets and reacted in air at 850 °C for 24 h.

For LiNiO_2 , an equimolar mixture of NiCO_3 and LiNO_3 was well mixed and pressed into pellets. The bright green pellets were predried in air at about 150 °C for 12 h in air and heated at 600 °C for 16 h under an oxygen stream. The precalcined black mixture was ground, pressed into pellets, and then reacted at 750 °C for 24 h under an oxygen stream.

$\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ [19] was prepared by heating the mixture of TiO_2 (anatase, Wako Pure Chemical Ind., Ltd., Japan) and $\text{LiOH}\cdot\text{H}_2\text{O}$ ($\text{Li}/\text{Ti} = 4/5$ in molar ratio) at 800 °C for 12 h under a nitrogen stream.

The reaction products thus obtained were ground and stored in a desiccator over blue silica gel and used for electrochemical tests without washing with distilled water. Natural graphite (NG-7, The Kansai Coke and Chemicals Co., Ltd., Japan) and bismuth (99.9% purity, Wako Pure Chemical Ind., Ltd., Japan) were used as received.

The electrochemical cells and the data acquisition system used in this study are the same as described in a previous paper [3]. The composition of electrode was 88 wt.% target sample, 6 wt.% acetylene black, and 6 wt.% Teflon binder (Teflon 30J, Du Pont-Mitsui Fluorochemicals Co., Ltd., Japan) except for graphite electrode which consisted of 97 wt.% graphite and

3 wt.% Teflon binder. All procedures for handling and fabricating the cells were performed in an argon-filled glove box. Other experimental conditions are given in Section 3.

3. Results and discussion

Fig. 1 shows almost steady voltage profiles for charge and discharge of (a) LiCoO_2 , (b) LiNiO_2 , and (c) $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ at a rate of 0.17 mA cm^{-2} at 30°C . In measuring charge and discharge curves lithium metal was used as a negative electrode. Mid values between average voltages for charge and discharge were about (a) 3.9 V, (b) 3.8 V, and (c) 1.55 V. Coulombic efficiencies for charge and discharge were (a) 97.5%, (b) 98.5%, and (c) about 100%. For LiCoO_2 and LiNiO_2 charge/discharge coulombic efficiencies depend on the degree of oxidation [3,20] or on the level of operating voltage. The cells operating at higher voltages generally show lower coulombic efficiencies, suggesting that the rate of electrolyte oxidation is a function of the electrode potential. For $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ coulombic efficiency is independent of the degree of reduction because of its extremely flat voltage profile at about 1.55 V [20,21] where any ester-based organic electrolyte is stable.

Fig. 2 shows the charge and discharge curves of (a) bismuth and (b) natural graphite. Approximate operating voltages of bismuth and graphite were 0.8 and 0.15 V, respectively. Coulombic efficiencies for well breaking-in electrodes were 98% for both bismuth and graphite. For natural graphite the coulombic efficiency was about 100% when the cell was cycled at constant-capacity charge of 150 mAh g^{-1} , based on graphite weight, under a constant current of 0.17 mA cm^{-2} followed by constant-current discharge up to 2 V, 99%

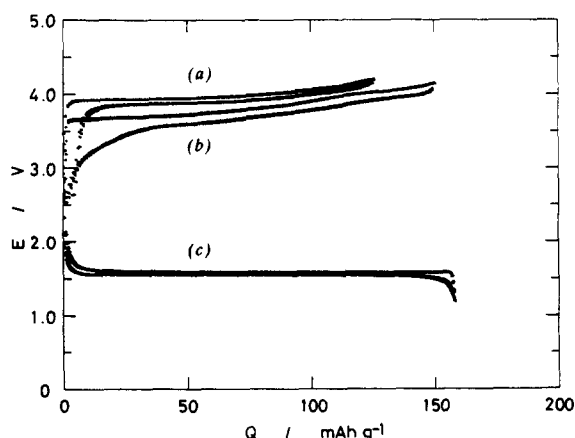


Fig. 1. Charge and discharge curves of (a) LiCoO_2 , (b) LiNiO_2 and (c) $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ in non-aqueous lithium cells at a rate of 0.17 mA cm^{-2} at 30°C . Electrolytes used were 1 M LiClO_4 dissolved in (a) propylene carbonate (PC), (b) PC, and (c) ethylene carbonate (EC)-1,2-dimethoxyethane (DME) (1:1 by volume).

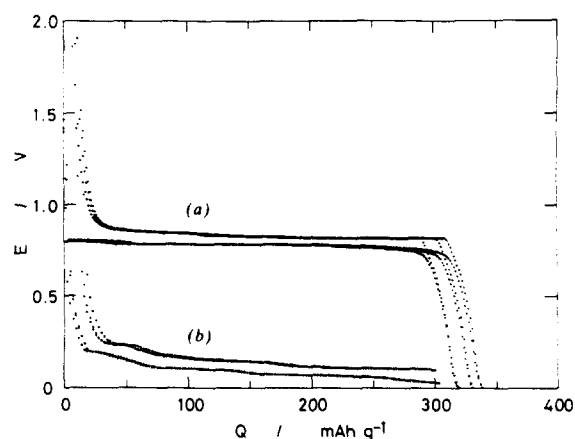


Fig. 2. Charge and discharge curves of (a) bismuth and (b) natural graphite (NG-7) in non-aqueous lithium cells at a rate of 0.17 mA cm^{-2} at 30°C . Electrolyte used was 1 M $\text{LiClO}_4/\text{EC-DME}$ (1:1 by volume).

at 250 mAh g^{-1} of charge capacity, and 98% at 300 mAh g^{-1} [15]. This suggests that the coulombic efficiency of the graphite electrode is also a function of the electrode potential of graphite.

Natural graphite (NG-7) and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ show excellent rechargeability [15,20,21]. LiCoO_2 and LiNiO_2 also show excellent rechargeability when they operate in voltages below 4.2 V, typically 4.15 V against a lithium electrode. If the end of the charge voltage is set above 4.2 V, then the rechargeable capacity rapidly fades during cycling [3,22]. Among these materials, we select natural graphite (NG-7) and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ as negative electrodes and LiNiO_2 as a positive electrode to fabricate lithium-ion cells.

Fig. 3 shows a lithium-ion cell consisting of LiNiO_2 and natural graphite (NG-7). Since the cell was fabricated in discharged state, open-circuit voltage of freshly prepared cell was about 0.08 V. In order to operate the lithium-ion cell without precharging to graphite electrode [15], the weight of each electrode material was adjusted empirically considering a loss of capacity during the first charge and discharge. The weight of samples loaded on a 3 cm^2 electrode was 0.085 g for LiNiO_2 and 0.037 g for natural graphite. In order to picture how the cell voltage will develop in the lithium-ion cell, the operating voltages for positive and negative electrodes were monitored with respect to an auxiliary lithium electrode during the constant-capacity charge (140 mAh g^{-1} based on LiNiO_2 weight) at 0.17 mA cm^{-2} and the constant-current discharge to 2.5 V of the terminal voltage for the lithium-ion cell. Since the loss of capacity during the first charge and discharge was adjusted to be the same value of about 70%, the cell can store and deliver electricity after the first cycle. As can be seen in Fig. 3, almost steady charge and discharge curves in terms of voltage profiles were obtained from the 2nd to 10th cycle. Crossing point in

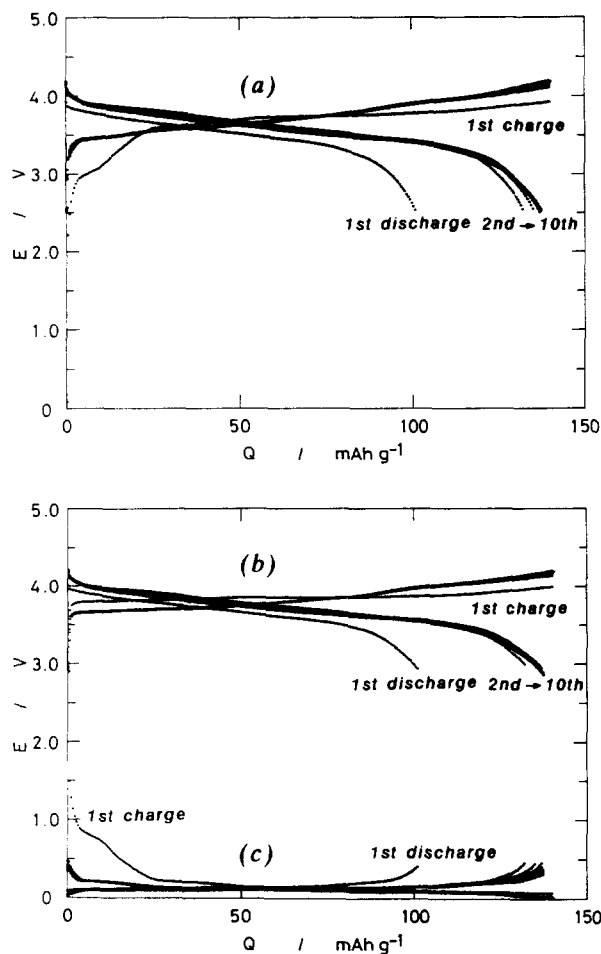


Fig. 3. Charge and discharge curves of a lithium-ion cell consisting of LiNiO_2 and natural graphite (NG-7) at a rate of 0.17 mA cm^{-2} at 30°C . To show how a lithium-ion cell works from the 1st to 10th cycle, operating voltages of (b) positive (LiNiO_2 : 0.085 g loaded on 3 cm^2) and (c) negative (natural graphite: 0.037 g on 3 cm^2) electrodes are shown with respect to an auxiliary lithium electrode in addition to (a) terminal voltages of a lithium-ion cell. Electrolyte used was 1 M LiClO_4 /ethylene carbonate (EC)–1,2-diethoxyethane (DEE) (1:1 by volume). Capacity in mAh g^{-1} was given based on LiNiO_2 weight.

voltages between charge and discharge is about 3.6 V. Voltage level in Fig. 3(a) is almost identical with that of an Li/LiNiO_2 cell. It is very difficult to measure real coulombic efficiencies for positive and negative electrodes in the lithium-ion cell. According to our results previously shown in the independent tests, charging and discharging the electrode materials above 3.5 V or below 1 V against a lithium electrode does not show 100% efficiency. Charge/discharge coulombic efficiency for each electrode is estimated to be about 98% for both LiNiO_2 and graphite. This equal loss of capacity for each electrode seems to make the lithium-ion cell cycleable without loss of rechargeable capacity while the coulombic efficiency is about 98% for the lithium-ion cell.

This is better illustrated in Fig. 4 for a lithium-ion cell consisting of LiNiO_2 and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$. The weight

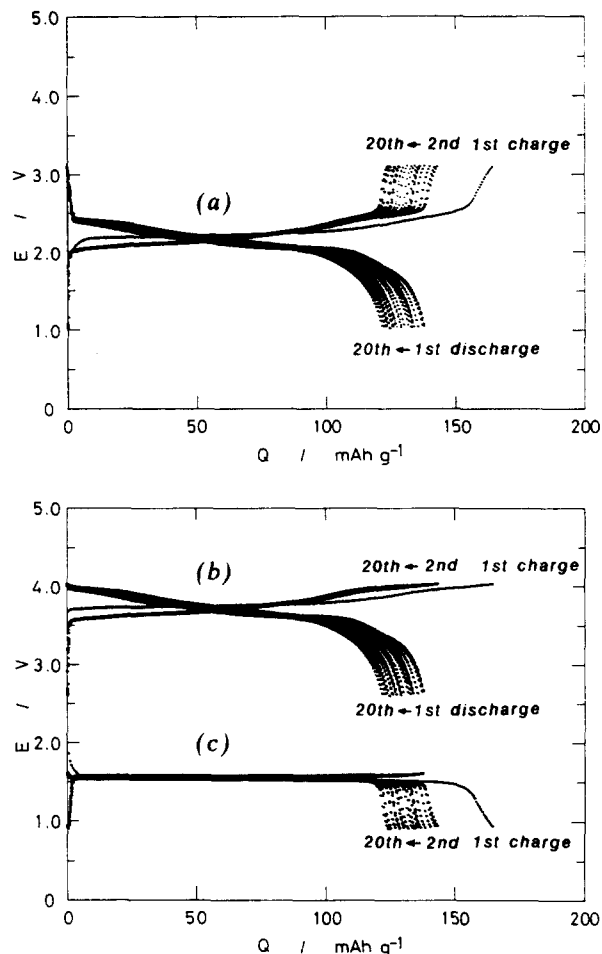


Fig. 4. Charge and discharge curves of a lithium-ion cell consisting of LiNiO_2 and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ at a rate of 0.17 mA cm^{-2} at 30°C . To show how a lithium-ion cell works from the 1st to 20th cycle, operating voltages of (b) positive (LiNiO_2 : 0.085 g loaded on 3 cm^2) and (c) negative ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$: 0.080 g on 3 cm^2) electrodes are shown with respect to an auxiliary lithium electrode in addition to (a) terminal voltages of a lithium-ion cell. Electrolyte used was 1 M LiClO_4 /EC–DME (1:1 by volume). Capacity in mAh g^{-1} was given based on LiNiO_2 weight.

of each sample loaded on a 3 cm^2 electrode was 0.085 g for LiNiO_2 and 0.080 g for $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$. Capacity Q in Fig. 4 is given in mAh g^{-1} based on LiNiO_2 weight. The cell was cycled at a constant current of 0.17 mA cm^{-2} between 1.0 and 3.1 V of terminal voltage for the lithium-ion cell. The initial open-circuit voltages of positive (LiNiO_2) and negative ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) electrodes were 3.21 and 2.92 V, respectively, against an auxiliary lithium electrode. Accordingly, the terminal voltage of freshly fabricated cell was 0.29 V. Coulombic efficiency of the first cycle was observed to be about 85%. Since the loss of capacity during the first cycle is not the same for the positive and the negative electrodes, the negative electrode is always in its charged state after the first cycle. Consequently, the limit of charging for the lithium-ion cell is determined by the charging capability of the negative electrode

($\text{Li}_2[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ is the fully charged state) and the limit of discharging is determined by the discharging capability of the positive electrode (LiNiO_2 is the fully discharged state). During cycling, the rechargeable capacity of the lithium-ion cell decreases gradually by a factor of 0.99 for each cycle, which is the charge/discharge coulombic efficiency of the lithium-ion cell. This is due to the imbalance of coulombic efficiencies between the positive and negative electrodes. The efficiency for each electrode is estimated to be 98.5% for LiNiO_2 and about 100% for $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$. The difference in coulombic efficiencies between the positive and negative electrodes, about 1% in this case, causes a gradual degradation of the rechargeable capacity even when the electrode materials are not damaged by charge and discharge cycles. When the coulombic efficiencies for the positive and negative electrodes are a function of the depth of charge to be operated and if the efficiencies of positive and negative electrodes can converge, rechargeable capacity of a lithium-ion cell will level off at a certain value. It is not the case in a lithium-ion cell consisting of LiNiO_2 and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ that the rechargeable capacity levels off during cycling, because the efficiency for negative ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) electrode is about 100% independent of the depth of charge as was described above.

4. Summary

In this paper we have briefly described a factor affecting the rechargeable capacity of a lithium-ion cell. The oxidation- and reduction-resistive electrolytes are necessary to improve the charge/discharge coulombic efficiencies of both the positive and negative electrodes to the values as close as 100%. However, the most important thing about the electrolyte properties is that the voltage window of an electrolyte fits with the operating voltages for positive and negative electrodes, such that coulombic efficiencies of both electrodes will converge and the state of charge for each electrode is adjustable by an electrolyte oxidation or reduction making a lithium-ion cell possible to operate for thousands of cycles. Electrochemical studies on the oxidation and reduction of electrolytes combined with the chemical analysis of reaction products will help to predict in advance cycle life and safety for a lithium-ion cell. Such an approach is in progress in our laboratory together with the research on materials for advanced batteries.

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