

Lithium Isotope Effects upon Electrochemical Release from Lithium Cobalt Oxide to Non-Lithium Electrolyte Solution

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Lithium was electrochemically released from a lithium cobalt oxide (LiCoO_2) cathode to an ethylene carbonate-based organic electrolyte solution containing no lithium ions, and the change in the lithium isotope composition of the cathode was measured. The $^7\text{Li}/^6\text{Li}$ isotopic ratio of the electrode was practically unchanged before and after the 45%–62% lithium release, which meant that the lithium release accompanied no isotope preference. This result is quite contrastive to the previous one; when lithium was released to an organic electrolyte solution containing lithium ions, the $^7\text{Li}/^6\text{Li}$ ratio of the cathode became 1.018 to 1.033 times smaller than that before the release. It was induced that the kind of electrolyte solution controlled the attainment of the lithium isotope exchange equilibrium between the cathode and the electrolyte solution.

Key words: Lithium Ion Secondary Batteries; Lithium Cobalt Oxide; Lithium Isotope Effects; Charge Reaction.

1. Introduction

We have been working on lithium isotope effects in electrode reactions of lithium ion secondary batteries (LIBs) [1–7]. If large lithium isotope effects are present in those reactions, LIBs may be utilized as an apparatus for enrichment and separation of lithium isotopes. The electrode reactions of LIBs are classified into two groups: charge and discharge reactions. In charge reactions, lithium atoms in the composite oxide cathode are released into the electrolyte solution as lithium ions, and lithium ions in the electrolyte solution are inserted (intercalated) into the graphite anode as lithium atoms. We experimentally showed that the lighter isotope, ^6Li , is preferentially fractionated into the graphite anode from an electrolyte solution, a 1 : 2 v/v mixed solution of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) containing 1 M lithium perchlorate (EC/EMC/ LiClO_4) by the charge reaction [3]. This lithium isotope fractionation can be understood as a manifestation of equilibrium isotope effects between lithium atoms in graphite and lithium ions in the EC/EMC solvent. The equilibrium isotope effects in the chemical exchange reaction be-

tween two chemical species can be theoretically evaluated by calculating the reduced partition function ratios (RPFs) of the two species [8]. Using model lithium species imitating lithium in the electrolyte solution and the graphite phases and calculating their RPF values based on the molecular orbital theory, we were able to elucidate the lithium isotope effects at the graphite anode–EC/EMC/ LiClO_4 interface by the charge reaction [9], although the quantitative agreement between the calculated and experimental isotope effects is not necessarily satisfactory. We have also experimentally studied the lithium isotope effects at anode–electrolyte solution interfaces by the charge reaction using tin [1], tin oxide [2], iron-silicon composite oxide [4], gallium [5], zinc [6], and zinc sulfide [7] as the alternative of graphite.

We have also investigated the lithium isotope effects accompanying lithium release from the lithium-cobalt composite oxide (LiCoO_2 ; lithium cobalt oxide) cathode into the EC/EMC/ LiClO_4 by the charge reaction [10]. Unfortunately, the $^7\text{Li}/^6\text{Li}$ isotopic ratio of the lithium released into the electrolyte solution could not be measured. We found, however, that the $^7\text{Li}/^6\text{Li}$ isotopic ratio of the cathode after the lithium

release was smaller than that of the virgin material. This finding means that the heavier isotope, ⁷Li, was preferentially fractionated into the electrolyte solution at the LiCoO₂ cathode–EC/EMC/LiClO₄ interface by the charge reaction [10].

The lithium isotope fractionation observed at the LiCoO₂ cathode [10] may also arise from equilibrium isotope effects like the fractionation at the graphite anode [3]. If this is the case, a large difference in the ⁷Li/⁶Li isotopic ratio, i. e., large lithium isotope effects, is expected between the cathode and the electrolyte solution by the charge reaction. In the previous paper [10], we measured the ⁷Li/⁶Li isotopic ratios of the cathode before and after the lithium release, and hence could estimate the change in the ⁷Li/⁶Li isotopic ratio accompanying the electrochemical lithium release. However, we could not determine the isotopic ratio of the lithium released to the electrolyte solution and consequently could not directly estimate the magnitude of lithium isotope effects between the cathode and the electrolyte solution, since the latter contained lithium ions from the beginning, the amount of which was much larger than the amount of the released lithium.

In the present study, we conducted experiments in which lithium atoms in the LiCoO₂ cathode were electrochemically released to a lithium-free electrolyte solution, a 1 : 2 v/v mixed solution of EC and EMC containing 1 M sodium perchlorate (EC/EMC/NaClO₄), so that we were able to directly measure the ⁷Li/⁶Li isotopic ratio of the released lithium. In this paper, we report the results of those experiments and discuss the difference in the lithium isotope effects between the LiCoO₂ cathode–EC/EMC/LiClO₄ and LiCoO₂ cathode–EC/EMC/NaClO₄ systems.

2. Experimental

2.1. Reagents

The cathode, which consists of an aluminum foil as an electrical current collector and fine powders of LiCoO₂ coated and pressed on the foil that function as active material, was purchased from Piotrek Co. Ltd. Its density, weight and capacity were 1.9 g/cm³, 13.4 mg/cm², and 1.5 mAh/cm², respectively. The anode, which consists of a copper foil as an electrical current collector and natural graphite powders coated and pressed on the foil that function as active material,

was also purchased from Piotrek Co. Ltd. Its density, weight and capacity were 1.1 g/cm³, 5.5 mg/cm², and 1.6 mAh/cm², respectively. The organic electrolyte solution (EC/EMC/NaClO₄) was manufactured by Tomiyama Pure Chemical Industry Ltd. The other reagents were of analytical grade and were used without further purification except for hexane, which was used after dehydration with molecular sieves.

2.2. Electrochemical Release of Lithium from the Cathode into the Electrolyte Solution

The experimental setup and procedure were the same as those of the previous paper [10] except that the electrolyte solution used was the EC/EMC/NaClO₄ instead of the EC/EMC/LiClO₄.

The experimental apparatus used is schematically drawn in Figure 1. It is composed of a power supply (a Hokuto Denko Corp. 201B battery charge/discharge unit), a two-electrode electrochemical cell (electrolytic cell), and a data acquisition unit consisting of an A/D converter and a personal computer (not shown in Fig. 1). The volume of the electrolyte solution placed in the cell was 12 cm³. The anode and cathode both with the size of 1 cm times 1 cm, were placed in the face-to-face position in the cell, after reinforced by a stainless steel mesh, so that the LiCoO₂ and graphite were wholly immersed in the electrolyte solution. The electrolytic cell was built up in a dry argon atmosphere.

The lithium release from the LiCoO₂ electrode was performed in a constant-current constant-voltage (CC-CV) mode. That is, the electrolysis (lithium release) was at first carried out in a constant current mode (1 mA). As it proceeded, the voltage difference between the two electrodes (cell voltage), which was initially nearly zero, gradually increased and reached the predetermined value set at 4.2 V. The electrolytic mode was then automatically changed to the constant

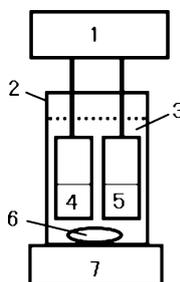


Fig. 1. Experimental apparatus. 1, charge-discharge controller (power supply); 2, electrolytic cell; 3, electrolyte solution; 4, LiCoO₂ cathode; 5, graphite anode; 6, stirrer tip; 7, magnetic stirrer.

voltage mode; the electrolysis was continued and the electric current gradually decreased while the cell voltage was kept at 4.2 V. The electrolysis was continued until the integrated quantity of electricity reached the predetermined value and was discontinued manually. The temperature of the electrolytic cell was kept constant at 25 °C during the electrolysis.

2.3. Chemical Analyses

After the electrolysis was finished, the cathode was taken out of the cell in a dry argon atmosphere, washed with dehydrated hexane and was allowed to stand for hours to remove the adhering hexane by evaporation. The lithium-released LiCoO₂ was recovered from the aluminum foil and heated at 700 °C for 3 h. The resultant lithium cobalt composite oxides were dissolved with 6 M hydrochloric acid (HCl), and the lithium and cobalt concentrations in the solution thus obtained were measured to obtain the amounts of lithium and cobalt in the cathode after the lithium release. The amounts of the metals before the electrolytic experiment were determined in a similar way using the virgin cathode material.

An aliquot of the electrolyte solution after the electrolysis was evaporated to dryness to remove the solvent (EC and EMC). The evaporation residue, which was basically a mixture of sodium and lithium perchlorates, was dissolved with distilled water. The solution thus obtained was added to a chromatographic quartz column (30 cm in length and 2 cm \varnothing in diameter), in which a cation exchange resin in the hydrogen form (Muromac 50W-X8, 200–400 mesh) was packed, and eluted with 0.5 M HCl to separate lithium from sodium [11]. The resin column height was 25.0 cm and the flow rate of the eluent was 4 cm³ min⁻¹. The 200–350 cm³ portion of the effluent which contained lithium ions but not sodium ions was collected. The lithium recovery was 96% or better. Using the lithium thus purified, the amount of lithium released to the electrolyte solution was calculated.

After the electrolysis was finished, the anode was also taken out of the cell in a dry argon atmosphere, washed with dehydrated hexane and was allowed to stand for hours to remove adhering hexane by evaporation. The lithium-inserted graphite was recovered from the copper foil and immersed in 0.1 M HCl overnight in order to stoichiometrically extract the inserted lithium and sodium. The amounts of lithium and

sodium inserted in the graphite anode were calculated by measuring the concentrations of lithium and sodium in the HCl solution thus obtained.

The sample preparation for the mass spectrometric measurement of the ⁷Li/⁶Li isotopic ratio of the lithium from LiCoO₂ was carried out as follows: A part of the lithium and cobalt-dissolved HCl solution was first evaporated to dryness. The evaporation residue was dissolved with distilled water, and the resultant solution was passed through a cation exchange column in the hydrogen form. Lithium ions trapped on the column were eluted out with 0.5 M HCl while cobalt ions stayed on the column. The former ions were thus separated from the latter ions. Lithium chloride from the cation exchange column was converted to lithium hydroxide through anion exchange and further converted to lithium iodide by the reaction with hydroiodic acid (HI). The lithium iodide thus prepared was subjected to the mass spectrometric analysis for the ⁷Li/⁶Li isotopic ratio. The purified lithium from the electrolyte solution was similarly subjected to the mass spectrometric analysis after the conversion to lithium iodide.

Concentrations of lithium and sodium in aqueous solutions were measured by flame photometry with a Thermo Electron SOLAAR M mkII atomic adsorption spectrometer, and that of cobalt by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments SPS7700 ICP-AES spectrometer, respectively. The ⁷Li/⁶Li isotopic ratios of the samples were determined by the surface ionization technique with a Finnigan MAT 261 mass spectrometer. The details of the ⁷Li/⁶Li isotopic ratio measurements were found in our previous paper [12].

2.4. Treatment of Lithium Isotopic Data

The magnitude of the lithium isotope effects upon the charge reaction at the cathode was evaluated by the following three factors:

The lithium isotopic variation factor, R , is defined as

$$R = ({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}} / ({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}, \quad (1)$$

where $({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}$ and $({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}}$ denote the ⁷Li/⁶Li isotopic ratio of lithium in the cathode after and before the lithium release, respectively. Both $({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}$ and $({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}}$ are experimentally determined quantities. The quantity R is a measure of the change in the lithium isotopic composition of the cathode upon the lithium release.

The observed lithium isotope separation factor, S , is defined as

$$S = \frac{({}^7\text{Li}/{}^6\text{Li})_{\text{A-electrolyte(obs)}}}{({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}}, \quad (2)$$

where $({}^7\text{Li}/{}^6\text{Li})_{\text{A-electrolyte(obs)}}$ is the measured isotopic ratio of the lithium released to the electrolyte solution. Both $({}^7\text{Li}/{}^6\text{Li})_{\text{A-electrolyte(obs)}}$ and $({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}$ are experimentally determined quantities.

The estimated lithium isotope separation factor, S' , is defined as

$$S' = \frac{({}^7\text{Li}/{}^6\text{Li})_{\text{A-electrolyte(calc)}}}{({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}}, \quad (3)$$

where $({}^7\text{Li}/{}^6\text{Li})_{\text{A-electrolyte(calc)}}$ is the lithium isotopic ratio of the released lithium calculated using $({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}}$, $({}^7\text{Li}/{}^6\text{Li})_{\text{A-cathode}}$ and the amounts of lithium in the cathode before and after the lithium release.

The quantity S' is related to R by

$$S' = \frac{m_{\text{B}} \times ({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}} \times (1 + R) - m_{\text{A}} \times (({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}} + 1)}{m_{\text{B}} \times (1 + R/({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}}) - m_{\text{A}} \times (({}^7\text{Li}/{}^6\text{Li})_{\text{B-cathode}} + 1)}, \quad (4)$$

where m_{B} and m_{A} denote the amounts of lithium in the cathode before and after the lithium release, respectively.

The quantities S and S' are the measures of the lithium isotope effects occurring at the LiCoO₂ cathode-EC/EMC/NaClO₄ interface. If every analysis is completely accurate, the value of S' should agree with that of S . By definition, R , S , and S' are all larger than unity when the heavier isotope of lithium is preferentially fractionated to the electrolyte solution.

3. Results and Discussion

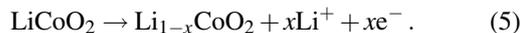
3.1. Mass Balance of Lithium

In the present study, five electrolytic experiments in the charge mode were conducted. In an experiment, lithium atoms in the LiCoO₂ cathode were released into the EC/EMC/NaClO₄ as lithium ions, and sodium ions in the electrolyte solution were inserted into the graphite anode as sodium atoms. A small portion of the lithium ions released may further have been taken up by the graphite anode.

The amount of lithium released from the LiCoO₂ cathode can be calculated from the change in the chemical composition of the LiCoO₂ cathode before and after the electrolysis. This should be equal to the sum of the amount of lithium in the electrolyte solution and that in the graphite anode found after the electrolysis. Chemical analyses showed that they agreed with each other within 1.1%–4.9% error, which indicated the satisfactorily high accuracy of the present chemical analyses.

3.2. Charge Reaction

In the present experiments, the occurring charge reaction is expressed as



The experimental conditions and results except for the isotopic data are listed in Table 1. The electrolysis time was varied from 1489 to 7232 s and the integrated quantity of electricity ranged from 1486 to 6096 mC. No apparent correlation of the integrated quantity of electricity with the electrolysis time was observed in spite of the fact that the experiments were conducted under similar experimental conditions. This may be attributable to such differences as those in the degree of occurrence of possible side reactions and in the surface area of LiCoO₂ particles among the experiments.

An example (Run N10) of the changes of the cell voltage and the electric current during the electrolytic course is shown in Figure 2. The cell voltage increased very quickly from the initial value of ca. zero at the very beginning of the electrolysis and then gradually approached the predetermined value of 4.2 V. After about 4200 s from the commencement of the electrolysis, it reached the predetermined value and was kept constant thereafter. The electric current was kept constant until the cell voltage reached the predetermined value and then started decreasing. It is clear that the EC/EMC/NaClO₄ can be used as an alternative to the EC/EMC/LiClO₄.

The Co/Li molar ratio after the electrolysis is larger than that before the electrolysis in every experiment.

Run No.	Electrolysis time / s	Integrated quantity of electricity / mC	Co/Li ratio after Li release ^c	Proportion of Li released / %	Current efficiency / %
N08	5403	3779	1.71	43.9	80
N09	7232	6096	4.19	77.1	113
N10	6004	5369	2.50	61.6	88
N11	6509	6048	3.88	75.2	103
N13	1489	1486	1.17	17.8	94

Table 1. Experimental conditions and results ^{a,b}.

^a The predetermined cell voltage was 4.2 V.

^b The predetermined electric current was 1.0 mA.

^c The Co/Li ratio of the cathode before Li release was 0.961.

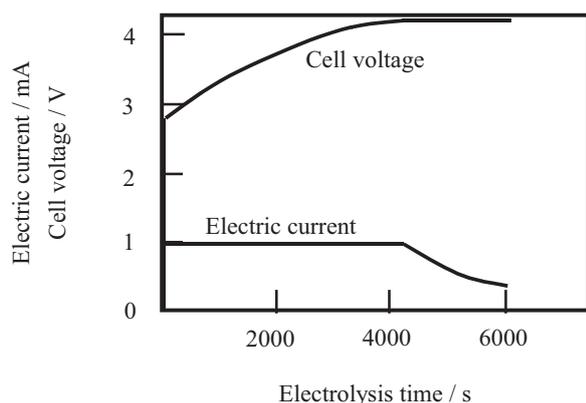


Fig. 2. Example of the cell voltage and the electric current changes as functions of the electrolysis time (Run N10).

The ratio of the amount of the released lithium to that in the virgin electrode (m_A/m_B) ranged from 0.18 to 0.77 (18 to 77%). The value of m_A/m_B very close to zero or unity is undesirable from the standpoint of the observation of the lithium isotope effects, since no lithium isotope effects will be observed at m_A/m_B equal to zero or unity. The range of the m_A/m_B value of 0.18 to 0.77 thus seems adequate to detect the lithium isotope effects that may occur.

The electric current efficiency (%), which is defined as 100 times the ratio of the amount of the released lithium to the amount that corresponds to the integrated quantity of electricity, ranged from 80 to 113%. Other than the experimental errors, a possible reason for the current efficiency less than 100% may be an insufficient hexane washing of the electrode after the electrolysis; a small portion of lithium ions in the electrolyte solution may have survived the hexane washing and have kept adhering to the surfaces of the LiCoO₂ particles, which certainly contributed to reducing the current efficiency. The current efficiency of similar exper-

iments with the EC/EMC/LiClO₄ in our previous paper [10] was low, ranging from 54 to 80%. This difference in the current efficiency may be attributable to the fact that concentrations of lithium were much higher in the experiments with the EC/EMC/LiClO₄ than with the EC/EMC/NaClO₄, and consequently, the contamination of the cathode by the adhering electrolyte solution is expected to be much larger for the former. The value of the current efficiency of more than 100% may be due to the experimental errors.

3.3. Lithium Isotope Effects

The isotope analysis was conducted on Runs N08, N09, N10, and N13. The values of R , S , and S' are summarized in Table 2, and in Figure 3, R (●) is plotted against the proportion of the released lithium given as $100 \times (m_B - m_A)/m_B$. The values of R obtained for the LiCoO₂-EC/EMC/LiClO₄ system (○) in the previous paper [10] are also shown for comparison. The value of R ranged from 1.000 to 1.010 in the present LiCoO₂-EC/EMC/NaClO₄ system. Runs N8, N10, and N13 have the R value of 1.000 and 1.001, which means that no lithium isotope fractionation occurred between the cathode and the electrolyte solution, and the value of 1.010 (Run N09) indicates a slight preferential fractionation of ⁷Li in the electrolyte solution. These values in the present study should be compared with 1.018–1.033, which is a clear indication of preferential fractionation of ⁷Li into the electrolyte solution, obtained for the LiCoO₂-EC/EMC/LiClO₄ system in the previous paper [10]. The difference between the two systems is much more clarified by comparing the estimated separation factor S' ; while it ranged from 1.000 to 1.014 in the present experiments, it was from 1.045 to 1.060 in the previous paper [10].

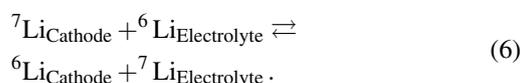
The large difference in the R value between the LiCoO₂-EC/EMC/LiClO₄ and LiCoO₂-EC/EMC/

Run No.	Proportion of Li released / %	⁷ Li/ ⁶ Li isotopic ratio of LiCoO ₂ before electrolysis	⁷ Li/ ⁶ Li isotopic ratio of LiCoO ₂ after electrolysis	⁷ Li/ ⁶ Li isotopic ratio of electrolyte after electrolysis	<i>R</i> ^a	<i>S</i> ^a	<i>S'</i> ^a
N08	41.6	12.508	12.500	12.480	1.001	0.998	1.002
N09	76.1	12.500	12.371	12.547	1.010	1.014	1.014
N10	60.1	12.563	12.466	12.569	1.000	1.008	1.000
N13	14.4	12.537	12.530	12.571	1.001	1.003	1.004

Table 2. Isotopic results.

^a See (1), (2), and (3).

NaClO₄ systems can be understood as follows. The lithium isotope effects observed in the LiCoO₂–EC/EMC/LiClO₄ system are considered to mostly originate from the lithium isotope exchange reaction between the cathode and the electrolyte solution near the LiCoO₂–EC/EMC/LiClO₄ interface,



In (6), ⁿLi_{Cathode} denotes the lithium isotope (*n* = 6 or 7) remaining in the cathode and ⁿLi_{Electrolyte} denotes that released to the electrolyte solution. Li_xCoO₂ (0 < *x* ≤ 1) has a layered structure [13, 14]; lithium atoms are located between layers formed by cobalt and oxygen atoms, surrounded by oxygen atoms, and are expected to be mobile. Since lithium atoms in LiCoO₂ are mobile, it is probable that lithium atoms in LiCoO₂ and lithium ions in the electrolyte are isotopically in equilibrium with each other near the solid–solution interface. In addition, since lithium atoms are mobile in close-packed oxygen arrays [13, 14], they are considered to be more loosely bound in LiCoO₂ than lithium ions in the electrolyte solution in which lithium ions are solvated by four EC molecules [15]. Based on the theory of equilibrium isotope effects [9, 16], the heavier isotope is preferentially fractionated into the more tightly bound state. That is, ⁷Li is expected to be enriched in the electrolyte solution phase, which agrees with the experimental results in the previous paper [10], albeit in a qualitative fashion.

Contrary to the previous LiCoO₂–EC/EMC/LiClO₄ system, the large majority of cationic species in the electrolyte solution is sodium ions, and lithium ions in the electrolyte solution phase are only those supplied from the LiCoO₂ cathode in the present LiCoO₂–EC/EMC/NaClO₄ system. In such circumstances, lithium ions released from the cathode will

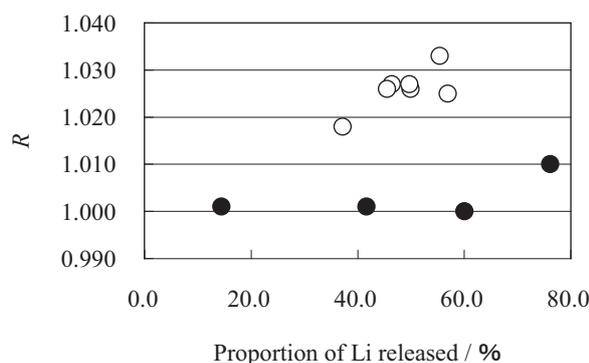


Fig. 3. Plot of *R* against the proportion of the released lithium. ●: present LiCoO₂–EC/EMC/NaClO₄ system, ○: previous LiCoO₂–EC/EMC/LiClO₄ system [10].

diffuse promptly into the whole solvent, and it is unlikely that the lithium isotopic equilibrium was attained between lithium atoms on the cathode and lithium ions in the electrolyte solution near the solid–solution interface. Thus in the present LiCoO₂–EC/EMC/NaClO₄ system, no equilibrium isotope effects based on (6) occurred. Lithium atoms were released sequentially starting from those near the surfaces of the LiCoO₂ particles of the cathode to those at core parts of the particles after being oxidized. This process is not accompanied by any lithium isotope effects.

Unlike the other experiments, Run N09 shows a slight preferential fractionation of the heavier isotope into the electrolyte solution phase. This can be regarded as a partial manifestation of the equilibrium isotope effects based on (6). The proportion of the released lithium is highest in Run N09 among the present experiments, and consequently, it is highly probable that the lithium isotopic equilibrium was attained between the cathode and the electrolyte solution in the latter part of the electrolytic course.

In the previous paper [10], we pointed out two possibilities that may explain the observed lithium isotope effects other than the one based on the equilib-

rium lithium isotope effects explained above. The first possibility is an uneven distribution of lithium isotopes within LiCoO₂ particles of the cathode. If the ⁷Li/⁶Li isotopic ratio is higher at the peripheral part of the LiCoO₂ particle than at the core, then it is possible that ⁷Li is seemingly preferentially transferred to the electrolyte solution phase. This possibility, however, can be ruled out by the present experiments. If this uneven distribution is the case, then the observed isotopic fractionation should be independent of the kind of electrolyte solution. Another possibility pointed out is a lithium isotopic difference in the easiness of oxidation at the cathode. If ⁷Li is more easily oxidized than ⁶Li, ⁷Li is released to the electrolyte solution more quickly. This leads to the preferential fractionation of ⁷Li to the electrolyte solution. This possibility is also ruled out, because the lithium isotope effects based on this phenomenon must also be electrolyte solution-independent.

4. Conclusion

To summarize the present study, we make the following statements.

A 1 : 2 v/v mixed solution of EC and EMC containing 1 M NaClO₄ can be used as electrolyte solution in

an apparatus imitating lithium ion secondary batteries as far as the first charging is concerned.

The lithium isotopic ratio of the lithium cobalt oxide cathode is nearly unchanged before and after the electrochemical release of lithium from the electrode to the electrolyte solution. It is in great contrast with the system in which an EC/EMC mixed solution containing 1 M LiClO₄ was used as the electrolyte solution; substantial depletion of the heavier isotope of lithium was observed on the cathode after the electrolysis. The large difference in the lithium isotope effects between the systems with the EC/EMC/LiClO₄ and with the EC/EMC/NaClO₄ is explainable by assuming that, while the lithium isotope exchange equilibrium was attained between the cathode and the electrolyte solution in the former system, this was not the case in the latter system.

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