Observation of Lithium Isotope Effects Accompanying Electrochemical Release from Lithium Cobalt Oxide

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This paper is dedicated to Professor Alfred Klemm on the occasion of his 100th birthday

Change in the lithium isotope composition in a lithium cobalt oxide (LiCoO$_2$) cathode for lithium ion secondary batteries accompanying the electrochemical lithium release from the cathode into an organic electrolyte solution was observed. The ^{7}Li/^{6}Li isotopic ratios of the electrodes after the release of 37.2 to 55.4% lithium were 1.018 to 1.033 times smaller than that before the release. This means that the heavier isotope, ^{7}Li, is preferentially transferred to the electrolyte solution.

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

1. Introduction

Naturally occurring lithium consists of two stable isotopes, ^{6}Li and ^{7}Li. ^{6}Li is expected to be employed as a blanket material for nuclear fusion reactors and ^{7}Li is used as a pH adjustor of coolants of nuclear fission reactors. Due to these important applications of lithium isotopes, enrichment and separation of the lithium isotopes has long been studied, and various methods for that purpose have been proposed.

We have investigated the method of lithium isotope separation based on lithium isotope effects accompanying electrode reactions of lithium ion secondary batteries [1 – 7]. These reactions may be categorized into two classes, i. e., charge and discharge reactions. In charge reactions, lithium atoms with the formal charge of 0 in lithium composite oxides cathodes are electrochemically released into an electrolyte solution as lithium ions, and lithium ions in the electrolyte solution are inserted (intercalated) into graphite anodes as lithium atoms with the formal charge of 0. In passing, in this paper, we use technical terms such as anode, cathode, and charge and discharge reactions by following the conventions in the research field of lithium ion secondary batteries; lithium composite oxides are cathodes, graphite is the anode, and the charge reac-tion is defined as the reaction in which lithium is released from the lithium composite oxides cathode. We found that the lighter isotope ^{6}Li is preferentially inserted in graphite upon charge reactions at anodes from an organic electrolyte solution [3]. Our molecular orbital (MO) calculations assuming equilibrium isotope effects between the electrolyte and graphite phases support the experimental results in a qualitative fashion [8, 9].

In place of graphite, we previously investigated tin [1], tin oxide [4], tin sulfide [7], iron–silicon composite oxide [4], gallium [5], and zinc [6] as anode material and measured magnitudes of lithium isotope effects by charge reactions. Like graphite, tin, gallium, zinc, and zinc sulfide preferred ^{6}Li over ^{7}Li. With tin oxide, the opposite lithium isotope preference was observed, while no lithium isotope effects were observed with iron–silicon composite oxide (within the experimental uncertainty). A factor controlling these varying isotope effects must be the difference in interactions between the inserted lithium atom with the formal charge of 0 and the atoms of the anode materials surrounding the lithium atom.

To the best of our knowledge, there is no study in the literature that reports lithium isotope effects at cathodes of lithium ion secondary batteries accompa-

nying charge reactions. In a large majority of lithium ion secondary batteries, lithium cobalt oxide, $LiCoO_2$, a stable lithium composite oxide with a layered structure, is used as the cathode material. As mentioned above, lithium is released as lithium ions from the lithium cobalt oxide into the electrolyte solution by the charge reaction. If this lithium release is accompanied by a lithium isotope effects, the lithium isotopic composition of the cathode should change before and after the lithium release. In the present study, we attempted to observe this lithium isotopic composition change experimentally, using commercially available $LiCoO_2$ electrodes for lithium ion secondary batteries, and in this paper, we report the results of such experiments.

2. Experimental

2.1. Reagents

The cathode, which consists of an aluminum foil as an electrical current collector and a fine powder of $LiCoO_2$ coated and pressed on the foil that functions as active material, was manufactured by Piotrek Co. Ltd. (PT-EdC15m-06X11-1-2 electrodes). Its density, weight, and capacity were $1.9 \, g/cm^3$, $13.4 \, mg/cm^2$, and $1.5 \, mAh/cm^2$, respectively. The anode, which consists of a copper foil as an electrical current collector and natural graphite powder coated and pressed on the foil that functions as active material, was also manufactured by Piotrek Co. Ltd. (Pixel A100 electrodes). Its density, weight, and capacity were $1.1 \, g/cm^3$, $5.5 \, mg/cm^2$, and $1.6 \, mAh/cm^2$, respectively. A 1 : 2 v/v mixed solution of ethylene carbonate (EC) and methylethyl carbonate (MEC) containing 1 M lithium perchlorate (LIPASTE-EC2MEC/1), used as organic electrolyte solution, was purchased from 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 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
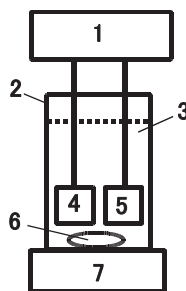

Fig. 1. Experimental apparatus. 1: charge–discharge controller (power supply), 2: electrolytic cell, 3: electrolyte solution, 4: $LiCoO_2$ cathode, 5: graphite anode, 6: stirrer tip, 7: magnetic stirrer.

cell) and a data acquisition unit consisting of an A/D converter and a personal computer (not shown in Figure 1). The amount of the electrolyte solution placed in the cell was $12 \, cm^3$. 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 $LiCoO_2$ and the graphite were wholly immersed in the electrolyte solution. The electrolytic cell was built up in a dry argon atmosphere.

The lithium release from the $LiCoO_2$ electrode was performed in the constant current–constant voltage (CC–CV) mode. That is, the electrolysis (lithium release) was at first carried out in the constant current mode (1 mA). As it proceeded, the electric voltage difference between the two electrodes (cell voltage), which was initially about zero, increased and reached the predetermined value of 4.2 V. The electrolytic mode was then automatically changed to the constant voltage mode; the electrolysis was continued and the electric current gradually decreased while keeping the cell voltage at the predetermined value. 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 $25 \, ^\circ C$ throughout the electrolysis.

2.3. Chemical Analyses

After the electrolysis was over, 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 adhering hexane by evaporation. The lithium-released $LiCoO_2$ was recovered from the aluminum foil and heated at $700 \, ^\circ C$ for 3 h. The resultant lithium cobalt composite oxides was dissolved with 6 M hydrochloric acid, and the lithium and cobalt concentrations in the solution thus obtained was 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.

The sample preparation for the mass spectrometric analysis for the ^{7}Li/^{6}Li isotopic ratio was carried out as follows: A part of the lithium and cobalt-dissolved hydrochloric 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 hydrochloric acid 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. The lithium iodide (I is monoisotopic) thus prepared was subjected to the mass spectrometric analysis for the ^{7}Li/^{6}Li isotopic ratio.

Lithium and cobalt concentrations in solutions were measured by flame photometry with a Thermo Electron SOLAAR M mkII atomic adsorption spectrometer and by ICP-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments SPS7700 ICP-AES spectrometer, respectively. Powder X-ray diffraction (XRD) patterns of LiCoO$_2$ samples before and after the electrolysis were recorded using a Rigaku RINT 2100V/P X-ray diffractometer with Cu K_α radiation in the 2θ range of 5 to 80° at room temperature. Scanning electron microscopy (SEM) photographs were taken with a Hitachi S-4500 scanning electron micrometer.

The ^{7}Li/^{6}Li isotopic ratios of the samples were determined by the surface ionization technique with a Finnigan MAT261 mass spectrometer. The details of the ^{7}Li/^{6}Li isotopic ratio measurements are found in our previous paper [10].

2.4. Lithium Isotopic Data Treatment

The degree of variation in the ^{7}Li/^{6}Li isotopic ratio in the lithium cobalt oxide cathode upon lithium release is expressed by the lithium isotopic variation factor, R, defined as

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

where $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-cathode}}$ denotes the ^{7}Li/^{6}Li isotopic ratio of lithium in the cathode after the lithium release

and $\left(^7\text{Li}/^6\text{Li} \right)_{\text{B-cathode}}$ denotes that before the lithium release. Both $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-cathode}}$ and $\left(^7\text{Li}/^6\text{Li} \right)_{\text{B-cathode}}$ are experimentally determined quantities. The lithium isotopic separation factor, S, in the present experiments, is defined as

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

where $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-electrolyte}}$ is the isotopic ratio of the lithium released to the electrolyte solution and $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-cathode}}$ is that remaining in the cathode. The $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-electrolyte}}$ cannot be measured experimentally with the present experimental set-up but is calculated using $\left(^7\text{Li}/^6\text{Li} \right)_{\text{B-cathode}}$, $\left(^7\text{Li}/^6\text{Li} \right)_{\text{A-cathode}}$, the amounts of lithium in the cathode before and after the lithium release. By definition, both R and S are larger than unity when the lighter isotope of lithium, ^{6}Li, preferentially remains on the cathode.

3. Results and Discussion

In the present experiments, lithium atoms in the LiCoO$_2$ phase are electrochemically released to the electrolyte solution phase. The occurring charge reaction is expressed as

$$\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li} + x\text{e}^- . \quad (3)$$
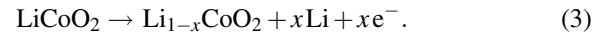
Seven electrolytic experiments were conducted. Experimental conditions and results are summarized in Table 1. The electrolysis (charge reaction) time ranged from 1.36 to 7.00 h, and the integrated quantity of electricity varied from 4.92 to 6.92 C.

An example of the changes of the cell voltage and the electric current during an electrolytic course (Run E01) is shown in Figure 2. The cell voltage increased swiftly at the beginning of the electrolysis and then gradually reached the predetermined value of 4.2 V after 1.47 h (5288 s) from the commencement of the electrolysis; it was kept constant thereafter. The electric current was kept constant (1 mA) until the cell voltage reached the predetermined value and then started decreasing with the rate of decrease being large at first and becoming gradually small. Thus, the electrolysis (charge reaction) was conducted in the CC–CV mode.

The mole ratio of cobalt to lithium, Co/Li, of the virgin LiCoO$_2$ material was found to be 0.961, although the theoretical value from its chemical formula is 1.0. For four out of seven experiments, the Co/Li ratio after the electrolysis was measured and found to be 1.59 to

Table 1. Experimental conditions and results [a, b].

Run No.	Electrolysis time / h	Integrated quantity of electricity / C	Co/Li ratio alter Li release[c]	Proportion of Li released / %	Current efficiency / %	^{7}Li/^{6}Li isotopic ratio before electrolyte		R	S
						LiCoO$_2$	Electrolyte		
E01	3.00	6.36	1.88	46	61	12.48	–	1.027	1.059
E02	2.01	5.97	1.85	46	54	12.48	–	1.026	1.058
E03	4.13	6.54	–	50	–	12.48	–	1.026	1.054
E04	7.00	6.37	–	50	–	12.51	12.43	1.027	1.055
E05	6.00	6.92	–	57	–	12.50	–	1.025	1.045
E06	4.31	6.47	2.24	55	80	12.50	12.46	1.033	1.060
E07	1.36	4.92	1.59	37	68	12.51	12.47	1.018	1.050

[a] The predetermined cell voltalte was 4.2 V.

[b] The predetermined electric current was 1.0 mA.

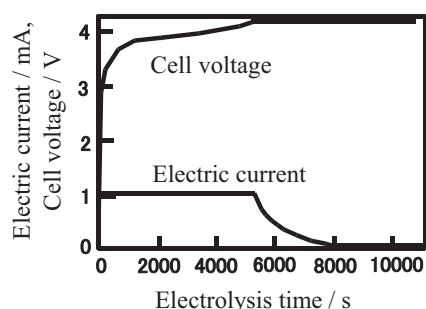[c] The Co/Li ratio of the cathode before Li release was 0.961.

Fig. 2. An example of the cell voltage and the electric current changes as functions of the electrolysis time.

2.24. The proportion of lithium released to the electrolyte solution was estimated to range from 37% to 57%.

The peak around $2\theta = 18°$ in the X-ray diffraction (XRD) pattern of the virgin LiCoO$_2$ cathode, which corresponds to the spacing of the adjacent (003) lattice planes of the LiCoO$_2$ crystal and was found at 18.96°, shifted to 18.38° for a cathode sample after the electrolysis of 6.54 C. This shift to the lower-degree side agrees with the known fact that, upon lithium release, the spacing of the (003) planes increases due to the increase in the electrostatic repulsion among oxygen atoms remaining in the crystal structure [11].

The electric current efficiency (%), defined as the amount of lithium depleted in the cathode during the electrolysis divided by the integrated quantity of electricity times 100, ranged from 54.0% to 80.3%. A possible reason for the current density less than 100% may be the incompleteness of hexane washing of the electrode after the electrolysis; lithium ions adhering to the surface of the LiCoO$_2$ cathode may have sur-

vived the hexane washing. Another plausible explanation was the occurrence of some reactions other than the oxidation of lithium atoms to lithium ions. The most probable candidate of such reactions is the electrolysis of water present as impurity in the electrolyte solution.
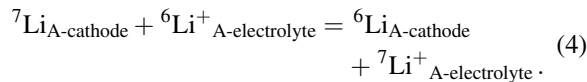
The R value ranged from 1.018 to 1.033, indicating that the heavier isotope, ^{7}Li, was preferentially released to the electrolyte solution and ^{6}Li tended to remain in the cathode during the charge reaction. The S value was estimated to be 1.045 to 1.060, which suggests that rather large lithium isotope effects are realized upon charge reaction at the interface of the LiCoO$_2$ cathode and the 1 M LiClO$_4$/EC/MEC electrolyte solution. The estimated S value of 1.045 to 1.060 is quite large compared to those observed for the charge reaction at the electrolyte/anode interfaces with a maximum value of 1.027 at 25 °C [2] and comparable to those reported for the amalgam method [12, 13].

In the present study, the lithium isotopic separation factor, S, was estimated indirectly using the R value and the proportion of lithium released to the electrolyte solution, instead of measuring the $(^7$Li/^{6}Li)$_{A\text{-electrolyte}}$ directly. Direct measurements of $(^7$Li/^{6}Li)$_{A\text{-electrolyte}}$ were impossible since the electrolyte solution contained 1 M lithium perchlorate, about 200 times denser than the concentration of lithium released to the electrolyte solution. We need an electrolyte solution that does not contain lithium in order to measure the $(^7$Li/^{6}Li)$_{A\text{-electrolyte}}$ experimentally, and we are now in the process of conducting electrolytic experiments in which lithium atoms are electrochemically released from the LiCoO$_2$ cathode to an organic electrolyte so-

lution (a 1 : 2 v/v mixed solution of EC and MEC) containing 1 M sodium perchlorate instead of 1 M lithium perchlorate.

In the present study, the heavier isotope of lithium was preferentially transferred from the LiCoO$_2$ cathode to the organic electrolyte solution accompanying the charge reaction (3). Three plausible origins for the observed lithium isotope fractionation are at present conceivable. The first plausible origin is an uneven distribution of lithium isotopic composition within LiCoO$_2$ particles of the cathode, although the possibility of its occurrence is considered to be very small. A SEM photo of the surface of a virgin cathode revealed that the sizes of the LiCoO$_2$ particles are about seven to fifteen μm. Assuming that the particle size is 10 μm and the proportion of the released lithium was 55%, then the result is that lithium atoms initially located up to 1.8 μm below the surface of a LiCoO$_2$ particle have been released. If the ^{7}Li/^{6}Li is higher at the peripheral part of the LiCoO$_2$ particle than at the core, then it is possible that ^{7}Li is seemingly preferentially transferred to the electrolyte solution phase. The determination of the vertical variation in the lithium isotopic composition within a LiCoO$_2$ particle may be possible by the secondary ion-microprobe mass spectrometry (SIMS) analysis.

The second plausible origin is the equilibrium lithium isotope effects between lithium atoms remaining in the LiCoO$_2$ and lithium ions released to the electrolyte solution. If the equilibrium constant, K_4, of the lithium isotope exchange reaction (4) below is larger than unity, then ^{7}Li is preferentially fractionated into the electrolyte solution phase and ^{6}Li to the LiCoO$_2$ phase:
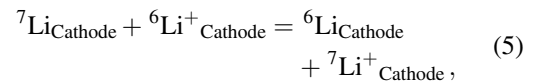
$$^7\text{Li}_{\text{A-cathode}} + {}^6\text{Li}^+{}_{\text{A-electrolyte}} = {}^6\text{Li}_{\text{A-cathode}} \\ + {}^7\text{Li}^+{}_{\text{A-electrolyte}} . \tag{4}$$

In (4), ^{i}Li$_{\text{A-cathode}}$ denotes lithium-i ($i = 6$ or 7) with the formal charge 0 in the LiCoO$_2$ phase, and ^{i}Li$^+_{\text{A-electrolyte}}$ denotes lithium-i with the formal charge of +1 released to the electrolyte solution phase. In this occurrence, we assume that the lithium isotope exchange reaction occurs between lithium atoms at and near surfaces of LiCoO$_2$ particles of the cathode and lithium ions in the electrolyte solution near the solid/solution interface and that the lithium isotope exchange equilibrium has been established throughout the electrolysis. Based on the theory of equilibrium isotope effects [14],

the preferential fractionation of ^{7}Li to the solution phase means that the sum of forces acting on lithium is stronger and consequently lithium is bound 'more stiffly' in the solution phase than in the solid (LiCoO$_2$) phase.

Our molecular orbital (MO) calculations for the solvation structure around the lithium ion in the EC/MEC mixed solvent revealed that the lithium ion is surrounded by four EC molecules in the mixed solvent; each EC molecule interacts with the lithium ion through its carbonyl oxygen atom [9]. On the other hand, each lithium atom in LiCoO$_2$ is surrounded by six oxygen atoms. Thus, lithium interacts with oxygen atoms in both phases. If the observed lithium isotope fractionation originates from the equilibrium isotope effects, then the difference in the strength of lithium-oxygen interaction between the two phases must account, in a good approximation, for the fractionation.

The third possibility is a lithium isotopic difference in the easiness of oxidation at the cathode. If ^{7}Li is more easily oxidized than ^{6}Li and the lithium ion in the LiCoO$_2$ crystal lattice can be released quickly from the lattice upon oxidation, then the consequence is that ^{7}Li is preferentially transferred to the electrolyte solution phase. Instead, we may think of a lithium isotope exchange reaction between lithium atoms and lithium ions within the LiCoO$_2$ crystal lattice:

$$^7\text{Li}_{\text{Cathode}} + {}^6\text{Li}^+{}_{\text{Cathode}} = {}^6\text{Li}_{\text{Cathode}} \\ + {}^7\text{Li}^+{}_{\text{Cathode}} , \tag{5}$$

where ^{i}Li$_{\text{Cathode}}$ denotes lithium-i ($i = 6$ or 7) with the formal charge 0, and ^{i}Li$^+_{\text{Cathode}}$ denotes lithium-i with the formal charge of +1 both in the LiCoO$_2$ phase. This equilibrium isotope exchange reaction, which can also be regarded as an electron exchange reaction, is different from (4) in that both lithium atoms and lithium ions are in the LiCoO$_2$ phase in (5). The equilibrium constant, K_5, of (5) larger than unity means that ^{7}Li is more apt to be oxidized.

The equilibrium constants K_4 and K_5 of (4) and (5) may be theoretically estimated by calculating ^{7}Li-to-^{6}Li isotopic reduced partition function ratios (RPFRS) [14] of lithium species involved in the isotope exchange reactions based on the MO theory. We have already obtained RPFRS values of the lithium ion in the EC/MEC mixed solution [8, 9]. To the best of our knowledge, no MO study on lithium isotopic RPFRS in the LiCoO$_2$ crystal lattice is reported. Al-

though it is in general difficult to estimate RPFRS in solid states based on MO calculations, periodic boundary conditions MO calculations [15] may be a possibility.

4. Conclusion

In an electrolytic cell consisting of a lithium cobalt oxide ($LiCoO_2$) cathode, a graphite anode, and an EC/MEC mixed solution containing 1 M lithium perchlorate, which is modelled on lithium ion secondary batteries, lithium in the cathode was electro-chemically released to the electrolyte solution (charge reaction). Lithium isotope fractionation in the cathode was observed to accompany the lithium release. The heavier isotope, ^7Li, was found to be more substantially depleted in the cathode than the lighter one, ^6Li, which

meant that ^7Li was preferentially transferred to the electrolyte and ^6Li tended to remain in the crystal lattice of $LiCoO_2$. The lithium isotopic variation factor, defined as the $^7Li/^6Li$ isotopic ratio of the cathode before the charge reaction (electrolysis) divided by that after the electrolysis ranged from 1.018 to 1.033 at 25 °C.

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