

Antifluorite compounds, $\text{Li}_{5+x}\text{Fe}_{1-x}\text{Co}_x\text{O}_4$, as a lithium intercalation host

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Abstract

Antifluorite-type materials, $\text{Li}_{5+x}\text{Fe}_{1-x}\text{Co}_x\text{O}_4$, were prepared and studied as a cathode for use in a lithium secondary battery. During the first charge process, the structure undergoes a phase change as the removal of lithium progresses. The original antifluorite structure is almost completely lost when 1.5 equivalents of lithium are deintercalated from the structure, as in the case of Li_5FeO_4 . This tendency was less obvious in cobalt-doped samples, and 2.1 equivalents of lithium could be removed before the original lattice disappeared. Cobalt doping helps to maintain the original lattice configuration and enhances cycling stability. The Mössbauer spectra suggest that the electrons of oxygen atoms play a role in addition to those of iron. A 1.3 equivalents of lithium could be reversibly deintercalated from $\text{Li}_{5.6}\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_4$, which corresponds to 220 mAh g⁻¹.

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1. Introduction

An important topic in practical electrode materials is the improvement of specific capacity. Some anode materials can produce a capacity of over 1000 mAh g⁻¹, while cathode materials generally produce only 100–200 mAh g⁻¹. Thus, an increase in cathode capacity should be quite effective for enhancing battery performance.

Another problem associated with a practical cathode of LiCoO_2 is the cost, due to the use of cobalt, which is relatively rare. Attempts have been made to develop a high-capacity cathode which contains an abundant low-cost element in place of cobalt.

A cathode material that contains iron is attractive from the perspective of both cost and non-toxicity. The LiFeO_2 compound exists in various crystal structures such as rock-salt, rock-salt super structure, layered structure, corrugated layer structure, hollandite type, etc. Some of these structures can

act as an intercalation host, but trials on the stably reversible extraction/insertion of a large amount of lithium have been unsuccessful. In 1971, Demoisson et al. found new lithium iron oxides, i.e., both high temperature and low temperature forms of Li_5FeO_4 , in mixtures of Li_2O and Fe_2O_3 [1]. Both forms exhibit an antifluorite-type structure, $\text{Li}_5\text{V}_2\text{FeO}_4$ (V: vacancy), in which both Li and Fe are located in tetrahedral sites and two equivalent vacancies are ordered among these tetrahedra. This structure is quite different from commonly studied octahedral materials with regard to the cationic conditions. The antifluorite structure is thought to be a good ionic conductor based on the fact that oxide ions in stabilized zirconia, which has a fluorite structure, show a high diffusion rate. The low- and high-temperature forms are isostructural to Li_5GaO_4 [2] and Li_6CoO_4 [3], respectively. FeO_4 tetrahedra show quite different configurations in the high- and low-temperature forms.

The structure of a practical graphite anode and a LiCoO_2 cathode can be described as a two-dimensional host. A representative three-dimensional host is LiMn_2O_4 , and the antifluorite material can also be classified in this category. In

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contrast to the spinel structure, the FeO_4 tetrahedra are not directly linked to each other and are isolated. The weak bonding between the FeO_4 tetrahedra enables them to be easily displaced with lithium intercalation, which may contribute to the high charge–discharge rates.

The theoretical capacity of the antiferite Li_5FeO_4 is 173 mAh g^{-1} with the intercalation of one equivalent of lithium. The cobalt antiferite Li_6CoO_4 can produce 326 mAh g^{-1} of capacity, since it can start from Co^{2+} to reach Co^{4+} . High lithium ion mobility and an easily modifiable valence of the transition metal can facilitate a high degree of reversible lithium intercalation. Based on these considerations, Takeda, who is one of the present authors, first proposed that an antiferite material with a formula of Li_5FeO_4 could be a new cathode candidate [4]. In this study, the electrochemical performance of this material was tested. The mechanism of intercalation was investigated using X-ray diffraction and ^{57}Fe Mössbauer spectroscopy was used to examine the oxidation state of iron during charge and discharge. Cobalt substitution in Li_5FeO_4 was also attempted and its effects on performance were examined.

2. Experimental

Li_5FeO_4 was synthesized using traditional ceramic methods from Li_2O (Kojundo Chemicals Laboratory Co., Japan) and $\alpha\text{-Fe}_2\text{O}_3$ (Nacalai Tesque Co., Japan). A mixture of Li_2O and Fe_2O_3 was pressed into tablets 8 mm in diameter in an argon atmosphere and heated in an electrical furnace at 900°C under a nitrogen stream. The low-temperature form was obtained by slowly cooling the product in the furnace from 900°C . Since the electrochemical performance of the high-temperature form is similar to that of the low-temperature form, we focus on the latter in this paper.

Since Fe_2O_3 is not very reactive, lithium evaporates before the reaction is complete. When lithium and iron are mixed in a stoichiometric ratio of 5:1, lithium always becomes deficient and LiFeO_2 is formed as an impurity. If excess lithium is added, Li_2O remains in the product. Thus, a 6:1 molar ratio of starting lithium and iron materials was used to obtain a single phase.

We tried to make a solid solution between Li_5FeO_4 and Li_6CoO_4 , because Li_6CoO_4 has a higher theoretical capacity. To improve the rate of the reaction, FeOOH was used as an iron source instead of Fe_2O_3 . Li_2O and $\text{Co}(\text{OH})_2$ were used as lithium and cobalt sources, respectively. With this combination, the stoichiometry of the product was the same as the starting ratio and no excess lithium was necessary. The mixture of these three components was calcined at 700°C for 8 h, then ground and palletized again. It was then annealed at 700°C under a nitrogen stream. The composition of the final product can be described as $\text{Li}_{5+x}\text{Fe}_{1-x}\text{Co}_x\text{O}_4$ ($0 < x < 1$).

X-ray diffraction (XRD) measurements were performed on a Rigaku RAD RC (12 kW) using monochromated $\text{Cu K}\alpha$ radiation. Since the products were hygroscopic, they were

protected against moisture during the XRD measurement by using a gas-tight holder filled with argon gas. A $7 \mu\text{m}$ thick aluminum window covered the sample holder plate in an arc. The Mössbauer effect is appropriate for examining the oxidation state of iron. The room-temperature Mössbauer spectra of charged or discharged samples were measured. The experimental cell was specially designed using laminated film as a container substance and quasi in situ measurements were carried out without opening the cell.

To test the charge–discharge performance as a cathode, a conventional coin-type cell was assembled. The oxide (50 mg) was ground and mixed with acetylene black (10 mg) as an electron conductor and Teflon (0.5 mg) as a binder, and the mixture was pressed into a tablet of 12 mm in diameter under a pressure of 1 MPa. The cell was assembled using this tablet as the cathode, a lithium sheet as the anode and 1 M $\text{LiClO}_4/\text{ethylene carbonate (EC) + diethylcarbonate (DEC)}$ as the electrolyte.

3. Results and discussion

The first several charge–discharge curves of Li_5FeO_4 are shown in Fig. 1. The electrochemical test was performed under a constant current density of 0.3 mA cm^{-2} . The cycle was repeated within a voltage range of 1.8–4.3 V with the additional cut-off condition that the process was terminated when the capacity reached 200 mAh g^{-1} . The first charging potential maintained a constant value at 3.5 V, which indicates a phase change as discussed later. In this antiferite structure, it should be noted that the FeO_4 tetrahedra are isolated from each other. When lithium is removed from adjacent sites surrounding a FeO_4 tetrahedron, it may be difficult to maintain the original crystal configuration like a layered host material. As a consequence of phase evolution, the curve shows a potential plateau from the beginning of a charge process. In a separate experiment, this potential plateau was found to continue until $x = 1.5$ (260 mAh g^{-1}), where x indicates

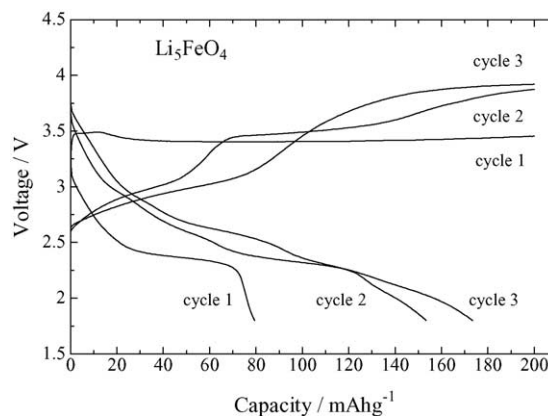


Fig. 1. Typical charge–discharge curves of Li_5FeO_4 . The current density was set at 0.3 mA cm^{-2} and each process was terminated by either capacity or voltage cut-off conditions; 4.0–1.8 V and 200 mAh g^{-1} .

an equivalent amount of lithium in $\text{Li}_{5-x}\text{FeO}_4$. Beyond this point, the potential begins to increase steeply and reaches 4.0 V at $x=2.0$. The fact that the further removal of lithium from the structure is accompanied by a large polarization suggests a limit to lithium deintercalation. Forced lithium deintercalation beyond $x=1.5$ leads to a significant loss of reversibility.

On the other hand, the discharge process shows a typical curve of decreasing potential. The difference between the charge and discharge potential profiles reflects an irreversible phase change. The structural change that the host structure undergoes during the charge process may be too large to be readily recovered during the discharge process. Lithium atoms experience different surroundings when they diffuse in the crystal structure during discharge. Lithium intercalation in the antifluorite material can be characterized as a non-topochemical reaction. The capacity of the first discharge process is estimated to be 80 mAh g^{-1} , indicating that the host can not accommodate the same amount of lithium delivered in the charge process. There are at least two possible explanations for this inconsistency between the capacities. First, from a kinetic perspective, the new phase may decrease the rate of diffusion of intercalated lithium, which could lead to large overvoltage. Second, from a thermodynamic perspective, the phase change may decrease the number of available lithium sites. Since this material can be thoroughly cycled under specific conditions, the latter possibility is most likely. Further studies will be needed to clarify the details.

The X-ray diffraction patterns of samples at several charge levels are shown in Fig. 2. The amount of deintercalated lithium ranges from $x=0$ to 2.0 in $\text{Li}_{5-x}\text{FeO}_4$. With an increase in x , the original peaks of the antifluorite structure become weaker, and almost disappear at $x=1.5$. Alternatively, two new peaks begin to appear near 45 and 65° and their intensities increase as charging progresses. The present results do not reveal the origin of these peaks. The simple pattern and the peak position may suggest a cubic structure. The most

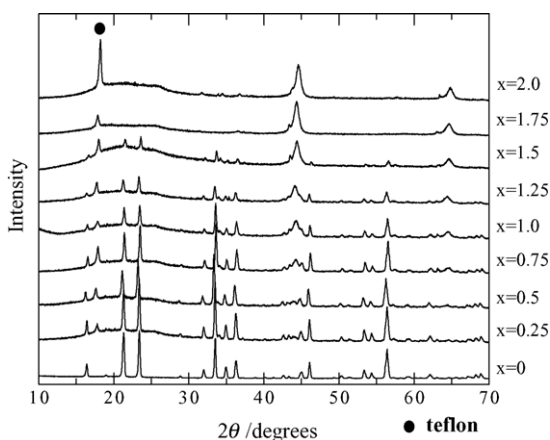


Fig. 2. XRD patterns of Li_5FeO_4 charged to 4 V (vs. Li) at the first cycle with a charge-transferred interval of 0.25 equivalents of lithium.

likely phase is considered to be $\alpha\text{-LiFeO}_2$, but the patterns do not adequately coincide.

The changes in the X-ray patterns clearly show that the potential plateau in the first charge process corresponds to a change from the original antifluorite structure to this new phase. This structural change is not reversible, as discussed above. Further removal of lithium beyond $x=1.5$ leads to complete extinction of the original pattern. This indicates completion of the structural change and the beginning of a single-phase region. In this new phase, intercalation does not show electrochemical reversibility. Therefore, it is important to stop the charge process before the composition becomes $\text{Li}_{3.5}\text{FeO}_4$ ($x=1.5$). In the phase mixture region, the new phase domains in the material's structure may obstruct lithium diffusion, but the coexisting original antifluorite domains can act as an intercalation host, so that reversible intercalation is considered to be maintained.

The change in the oxidation state of iron was examined by Mössbauer spectroscopy. The spectra of $\text{Li}_{5-x}\text{FeO}_4$ in the first cycle are shown in Fig. 3. The isomer shift (IS),

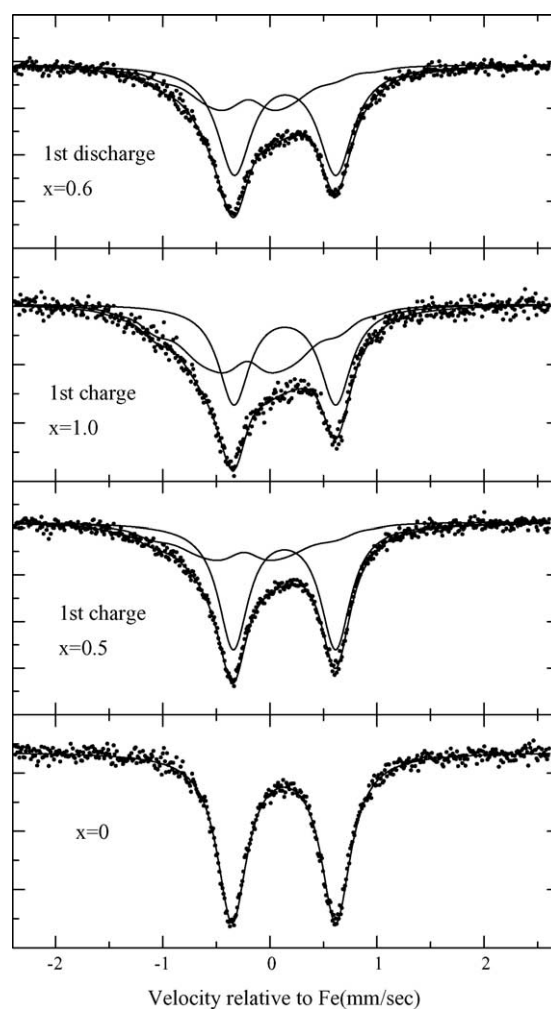


Fig. 3. Room-temperature ^{57}Fe Mössbauer spectra of Li_5FeO_4 in the first charge and discharge process. Observed data and calculated spectra are indicated by dotted and solid lines, respectively.

Table 1

Summary of the isomer shift and quadrupole splitting data derived from the spectra shown in Fig. 3

IS (mm s ⁻¹)	QS (mm s ⁻¹)	Peak area ratio (%)
<i>x</i> = 0 in Li _{5-x} FeO ₄		
0.13	0.96	100
First charge <i>x</i> = 0.5		
-0.24	0.92	34
0.13	0.96	66
First charge <i>x</i> = 1.0		
-0.21	0.89	53
0.14	0.95	47
First discharge <i>x</i> = 0.6		
-0.2	0.84	36
0.14	0.95	64

quadrupole splitting (QS) values and peak area derived from the spectra are summarized in Table 1. In the initial state before charging, the spectrum shows a doublet with an isomer shift of 0.13 mm s⁻¹. This is thought to correspond to Fe³⁺ in tetrahedral sites based on an analogy to Fe³⁺ in LiFe₅O₈ [5]. Upon charging, a new doublet peak appears at a much lower isomer shift of -0.24 mm s⁻¹. This low isomer shift indicates a higher oxidation state and is deduced to be Fe⁴⁺ from the reaction scheme. The existence of Fe⁴⁺ is supported by reports of Fe⁴⁺ in tetrahedral sites in Li_{1.2}Fe_{0.4}Ti_{0.4}O₂ [6] and Na₄FeO₄ [7], and of Fe⁴⁺ in octahedral sites in Li_xFe_{0.1}Ni_{0.9}O₂ [8]. Both systems show similar isomer shifts, so that it is difficult to distinguish the true configuration of iron ions in Li_{5-x}FeO₄. As charging progresses, the area of the Fe⁴⁺ doublet increases, and, alternatively, that of the Fe³⁺ doublet decreases. When one equivalent of lithium is charged, the formal valence of Fe must become four, as shown in the following equation:



However, the Mössbauer spectra show the coexistence of Fe³⁺ and Fe⁴⁺ states with similar peak intensities. With this result, the total valence at the end of charging can be calculated to be Fe^{3.5+}. One possible explanation is the existence of side reactions, but we believe no such reaction occurs, since charge and discharge occur at a moderate voltage range. Several other possibilities can also be considered, such as (1) the rest of the charge capacity is compensated by the oxidation of O_{2p} electrons [9], and (2) the formal valence of iron in the higher oxidation state is five rather than four.

Reversible behavior was observed in the discharge process, and the oxidation number of irons does not return to 3.0 at the end of discharge. This corresponds to the fact that the discharge capacity is less than the capacity of the preceding charge process. Overall, the changes in the Mössbauer spectra agree well with the electrochemical behavior.

The reversible capacity of Li_{5-x}FeO₄ under different cut-off conditions is shown against the cycle number in Fig. 4. In the case of *x* = 1.0, which corresponds to 173 mAh g⁻¹, 50 cycles were achieved without capacity fading. At the first

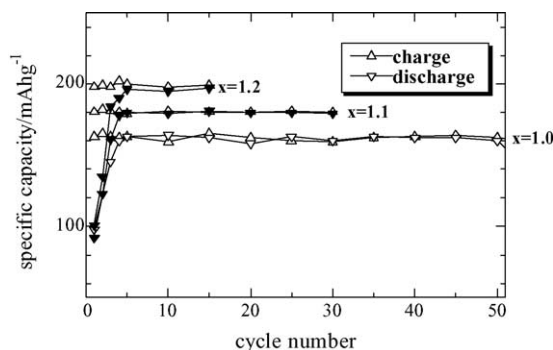
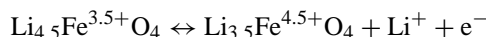


Fig. 4. Cycling performance of a Li/Li₅FeO₄ cell charged until *x* = 1.0, 1.1 and 1.2 in Li_{5-x}FeO₄ and discharged at a current density of 0.3 mA cm⁻².

discharge, about 40% of the capacity was not recovered. The discharge capacity increases with an increase in the cycle number, and finally the efficiency becomes 100% within a couple of cycles. If all of the charge transferred in these cycles is due to the extraction and insertion of Li⁺ for Li₅FeO₄, the reaction after five cycles can be expressed by the following equation in the case of *x* = 1.0,



As long as charging beyond *x* = 1.5 is avoided during the cycle, Li₅FeO₄ shows stable cycling behavior.

To improve the electrochemical performance, doping with another transition metal was attempted. In this study, cobalt was adopted as a substitute element, since the analogous antiferroite material Li₆CoO₄ is also known. Li₅FeO₄ and Li₆CoO₄ differ with regard to the arrangement of their FeO₄ tetrahedra. The chemical formula of a solid solution between Li₅FeO₄ and Li₆CoO₄ can be described as Li_{5+x}Fe_{1-x}Co_xO₄ and phase identification was carried out using X-ray diffraction analysis. The solid solution region exists at compositions near each end member. In the composition range of 0.3 < *x* < 0.5, the products become a two-phase mixture. Fig. 5 shows examples of the charge–discharge profiles of these products. The potential profiles are basically the same, but the discharge capacity gradually increases with an increase in the cobalt content. In the *x* = 0.6 sample, reversibility is significantly improved and the material produces 200 mAh g⁻¹ of reversible capacity. Among all the compositions tested, this ratio shows the best performance. When the cobalt content was increased beyond this composition, the material began to lose its reversibility again. An X-ray study showed that Li_{5.6}Fe_{0.4}Co_{0.6}O₄, which exhibits the best reversibility, exhibits higher resistance to a change in its structure upon the removal of lithium. Compared to Li₅FeO₄, the pattern of the original structure is more clearly maintained even after repeated cycles. When the charge process is continued, Li₅FeO₄ shows a rapid increase in potential from 260 mAh g⁻¹ as discussed above, while Li_{5.6}Fe_{0.4}Co_{0.6}O₄ shows this increase from a much higher capacity of 350 mAh g⁻¹. These data suggest that cobalt doping can help to improve the lattice stability,

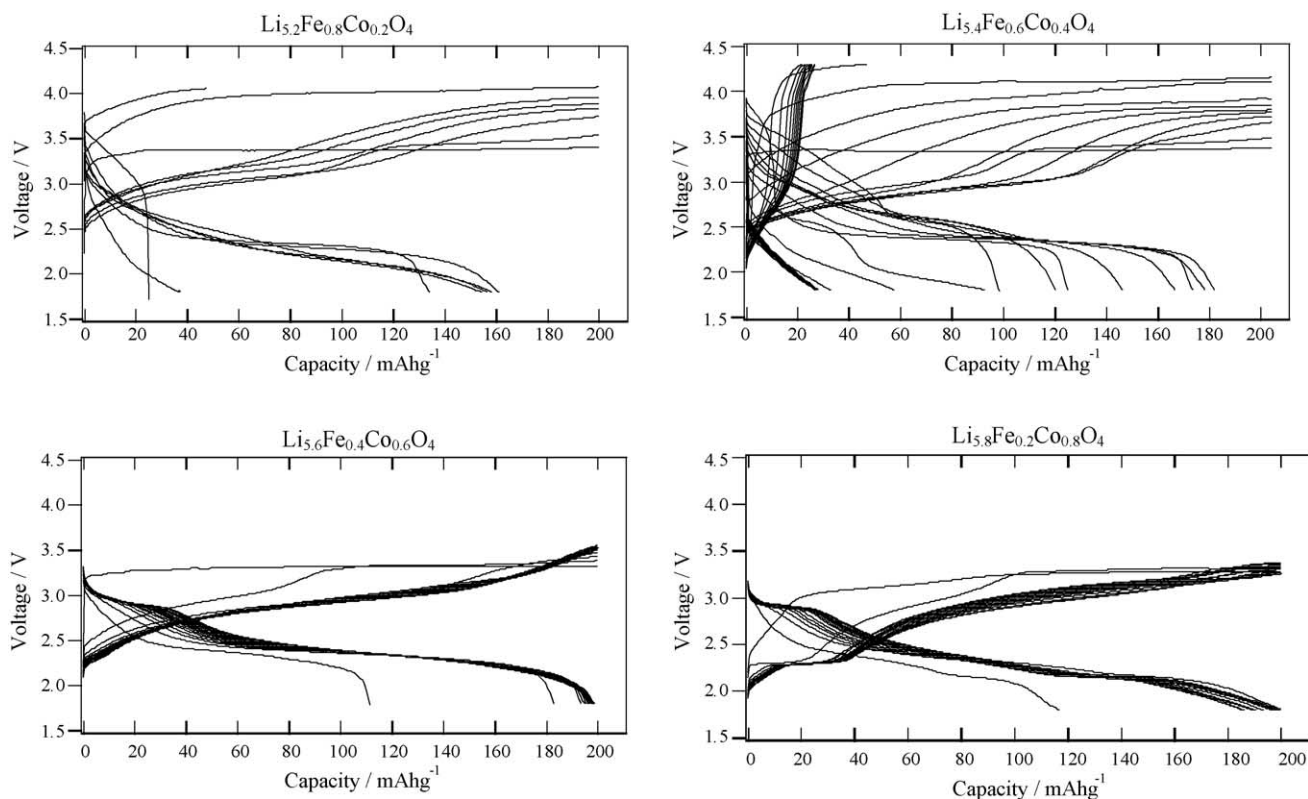


Fig. 5. The charge–discharge behaviors of cobalt-doped Fe-antiferroites $\text{Li}_{5+x}\text{Fe}_{1-x}\text{Co}_x\text{O}_4$ ($x=0.2, 0.4, 0.6,$ and 0.8). Each charge process was cut-off at 200 mAh g^{-1} and discharge was terminated at 1.8 V . The sample with $x=0.6$ shows the highest reversibility.

but cannot explain the relatively poor performance of Li_6CoO_4 . The reason for the change in reversibility with a change in the cobalt content should be clarified by further work.

The cycling ability of a $\text{Li}_{5.6}\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_4$ cathode was examined and the observed discharge capacities against the cycle number are presented in Fig. 6. Data were recorded for cells that run at charge cut-off capacities of 200 and

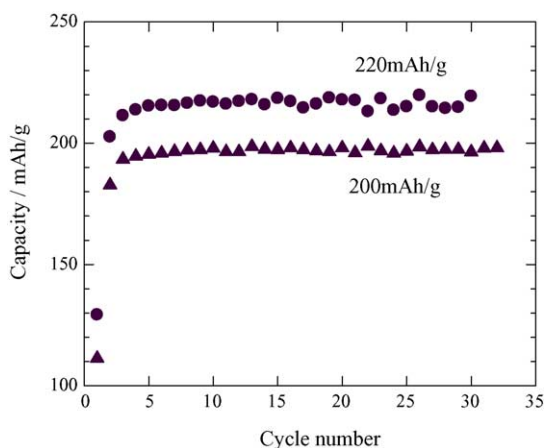


Fig. 6. Change in the discharge capacities of a $\text{Li}_{5.6}\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_4$ cathode at charge cut-off capacities of 200 and 220 mAh g^{-1} . The capacities are plotted against the cycle number.

220 mAh g^{-1} . Stable cycling was achieved for both cells and the reversible capacity of 220 mAh g^{-1} is a relatively high value among iron-containing cathodes. This reversible capacity corresponds to about 1.3 lithium atoms per unit formula. These results show that antiferroites may be suitable for use as a practical cathode material. Many variations can be synthesized and Li_6MnO_4 may be an interesting example. Manganese can take several valence states, which leads to a high theoretical capacity. When using antiferroites, it is probably most important to realize high structural stability. Further studies on this material are needed to identify better materials and to reveal the relation between the crystal structure and the mechanism of lithium intercalation.

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