

Oxidation Potential and Absolute Hardness Relationship in Lithium-ion Battery Electrolytes

Yoshiyuki MORITA¹Hiroto MAEYAMA¹Atsushi FURUKAWA¹

ABSTRACT

In this paper, we investigated the increase in oxidative stability of electrolytes in order to respond to the high-voltage operation of Li-ion rechargeable batteries. DFT geometry optimization calculations were performed for those molecular models of which side chain in the carbonate solvent substituted with a fluorinated alkyl group and the carbon in the main chain substituted with sulfur or oxygen. Linear correlation was found between the absolute hardness calculated from the frontier orbital energy following structural optimization and the oxidation potential determined by linear sweep voltammetry. Taking absolute hardness as an index, a mixed solvent of fluorinated alkyl ether and sulfolane, which was predicted to have better oxidative stability than carbonate solvent, was prepared as a prototype electrolyte. We then measured discharge capacity retention by a cyclic charge-discharge test using a battery with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which is a well-known cathode material for high-potential operation. The result showed that the number of cycles taken to reach a discharge capacity retention index of 80% increased from 45 cycles, which is the figure when using carbonate electrolyte, to 80 cycles, which is the prototype.

1. Introduction

The Nobel Prize in Chemistry 2019 was awarded jointly to Whittingham, Goodenough, and Yoshino for the development of and distribution of lithium-ion rechargeable batteries (LiB)⁽¹⁾. In addition to intercalation reaction, LiCoO_2 cathode, and graphite anode they proposed, a non-aqueous organic electrolyte for which Harris proposed the basic concept⁽²⁾ is an important part that constitutes LiB. A non-aqueous organic electrolyte (hereafter referred to as electrolyte) is a liquid where Li salt is dissolved in an organic solvent with the water content reduced to a part per million (ppm) level. It conducts Li ions between a cathode and an anode in charge-discharge reactions. Suppression of electrolysis of water by reduced water content achieves a cell voltage of 3 V or higher, contributing to a smaller and lighter LiB with high input⁽³⁾.

The main property that is required for electrolytes is a wide potential window and a high ion conductivity, which have an impact on the operation voltage and input/output properties of batteries⁽⁴⁾. To choose organic solvents with wide potential window among many types of organic solvents, electrochemical measurement results were accumulated since the 1970s, and solvents were chosen⁽⁵⁾⁻⁽⁹⁾. The result led to carbonate solvents being the main component of present electrolytes.

Measures for the higher energy density of LiB include

an increase in high-voltage operation and a higher capacity. Figure 1 shows the discharge curve of major cathode-active materials. Because the discharge plateau of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (hereafter referred to as LNMO4) is near

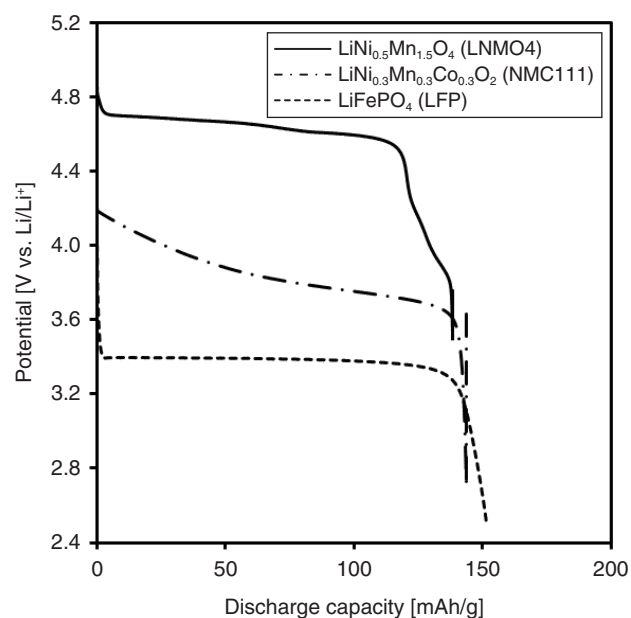


Fig. 1 Discharge curves for various cathodes

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4.7 V vs. Li/Li⁺, it has garnered attention as a cathode-active material that contributes to higher energy density. However, charge-discharge reactions that occur at a potential of about 1.0 V higher than the LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ cathodes that are in use today, oxidatively decompose electrolytes, leading to lower cycle performance⁽¹⁰⁾; thus, organic solvent with a higher oxidation potential than the carbonate solvent is desired.

2. Searching for Materials with Computational Science

Recent increase in accuracy and speed of material search methods in conjunction with computational science is phenomenal⁽¹¹⁾⁻⁽¹³⁾. If a calculation index that is correlated to material properties of interest is identified, target materials can be automatically screened. In terms of the oxidation potential of organic solvent, which is the main topic of the present study, a method exists that determines the oxidation-reduction potential by approximating the difference between total energy of the oxidized form and total energy of the reduced form to the standard chemical potential difference⁽¹⁴⁾. To screen numerous organic molecules, a method with less calculation burden is desired. Thus, the authors focused on the frontier orbit of organic solvent molecules and obtained the absolute hardness (η) as the material search index from the energy of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

Pearson examined a formulation based on the frontier orbit theory in terms of the degree of resistance of reactive species to chemical reactions; that is, hardness and proposed η shown in Eq. (1)^{(15), (16)}.

$$\eta = (I - A) / 2 \\ = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (1)$$

I and A are the first ionization energy and electron affinity of molecules, respectively. According to Koopmans' theorem⁽¹⁷⁾, I can be approximately replaced with the energy level of HOMO (E_{HOMO}) and A can be replaced with the energy level of LUMO (E_{LUMO}); thus, the median of the energy difference of the molecular frontier orbit (HOMO-LUMO Gap: ΔE) is η . Parr et al. verified that a larger η implies more thermal stability for molecules⁽¹⁸⁾. There are reports predicting color reaction for a photographic coupler that uses η as an index of chemical reaction⁽¹⁹⁾ and antioxidant performance of phenols⁽²⁰⁾. In the present study, we verified the correlation between η of organic solvent obtained from the electronic state calculation based on the density functional theory (hereafter referred to as DFT geometry optimization) and the actual oxidation potential, and prepared a prototype electrolyte with the organic solvent only, for which oxidative stability was predicted to enhance. The effectiveness of estimating oxidative stability by η was verified by the charge-discharge cycle performance of LNM04.

3. Calculation and Experimental Methods

3.1. Calculating the E_{HOMO} and E_{LUMO} Energy of Organic Solvents

Figure 2 shows the molecular structure of target organic solvents. Initial structures of ethylene carbonate [Fig. 2(a), R₁ to R₄ are hydrogen, noted as EC hereafter] and dimethyl carbonate [Fig. 2(b), R₁ and R₂ are methyl groups, noted as DMC hereafter]. We created a virtual molecular model where side chain extension (CH₃, C₂H₅, and C₃H₇) for R₁ to R₈, fluorinated alkyl group substitution (CH_xF_{3-x}, C₂H_yF_{5-y}, C₃H_zF_{7-z}, x = 1 to 3, y = 1 to 5, and z = 1 to 7), and O and S substitution of the main carbon chain were performed to these initial structures [Figs. 2(c-1) to (c-3)]. The objective of the fluorine substitution is to reduce the electron density of the carbonate by introducing a fluorinated alkyl group as a substitution with a strong electron acceptance rate. It creates an electronic state wherein it will be less likely for the cathode to accept electrons; that is, less likely to oxidize. To create a molecular model, we used the Pipeline Pilot by Accelrys. Virtual molecules were automatically created by combining the above substituents, which was followed by structural optimization and calculation of E_{HOMO} , E_{LUMO} , and η . For structural optimization, we used DFT geometry optimization package DMol^{3(21), (22)} by Accelrys. We used the Generalized Gradient Approximation (GGA) as the exchange-correlation function and Double numerical basis set with polarization function (DNP) as the basis-set. Comparison of BOP⁽²³⁾, PW91⁽²⁴⁾, and BLYP^{(25), (26)} for E_{HOMO} of ethylene carbonate found that their difference was about 0.2 eV; thus, we chose BLYP with many reports as the exchange interaction term. The calculation of the convergence condition was 10⁻⁶ Hartree.

3.2. Measurement of Oxidation Potential by Linear Sweep Voltammetry

Among the solvent molecules calculated in Section

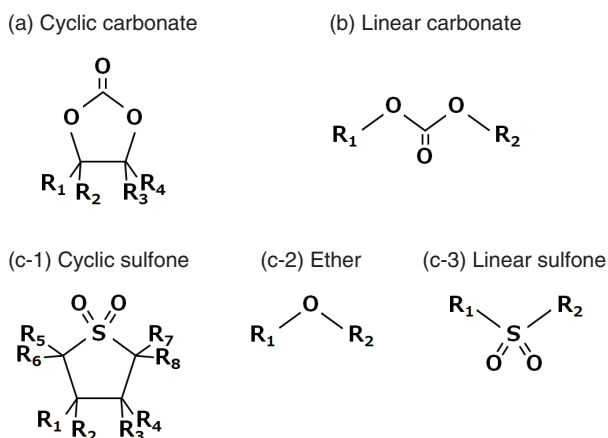


Fig. 2 Schematic illustration of organic solvent molecules

3.1., we performed linear sweep voltammetry (LSV) for solvents that could be synthesized or procured. We dissolved 0.1 mol/L of lithium hexafluorophosphate (LiPF_6) in the target organic solvent and added 2.0 mL into the electrochemical cell shown in Fig. 3. Linear carbonate [dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC)], and fluorinated alkyl ether (FAE) did not fully dissolve LiPF_6 ; thus, we prepared a solvent with 10 vol% of propylene carbonate (PC) and fully dissolved LiPF_6 . The working electrode was a platinum plate (The Nilaco Corporation, purity of 99.98%, diameter of 10 mm, and thickness of 0.1 mm) polished with an emery-paper (3M, 3000 grit). For the counter electrode and reference electrode, we used metallic lithium (Honjo Metal Co., Ltd., purity of 99.9% and thickness of 0.1 mm). For the separator, a microporous polyolefin membrane (Celgard 2500) was used. The prepared electrochemical cell was placed in a constant temperature bath with a temperature of 25°C. Solartron Analytical potentiometer/galvanostat 1287/1255 was used in scanning, with the scanning speed of 0.5 mV/sec. from the open circuit potential (OCP) to 7.0 V vs. Li/Li^+ . The oxidation potential was defined as an intercept of the slope of oxidation current against the LSV scanning baseline.

3.3. Preparation of an LNMO4 Cathode Composite Sheet

LNMO4 was synthesized with the solid phase method under the existing manufacturing conditions⁽²⁷⁾. For the synthetic layer of the cathode, ink in a slurry state dispersed in the *n*-methylpyrrolidone (NMP) solvent with a weight ratio of LNMO4: conductive material: binder = 91: 4: 5 was painted on an aluminum foil to prepare a sheet. The conductive auxiliary agent was acetylene black of Denka Company Limited, and the binder was polyvinylidene fluoride of Kureha Corporation that was dissolved in an NMP solution. The cathode composite sheet was pressed so that the electrode density would be 3.0 g/mL and punched with a diameter of 14 mm.

3.4. Electrochemical Test that Uses LNMO4

The charge/discharge reversibility of LNMO4 cathode was confirmed by changing the working electrode of the LSV measurement configuration (Fig. 3) from the platinum plate to the cathode composite sheet, and then using cyclic

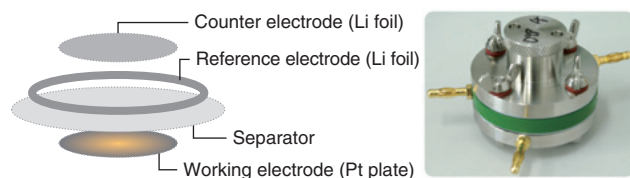


Fig. 3 Schematic illustration and cell appearance of three-electrode cell used for LSV

voltammetry (CV). The scanning rate was 0.5 mV/sec. and the potential range was 2.5 V to 5.4 V vs. Li/Li^+ . For charge-discharge cycle performance, we sealed a cathode composite sheet, separator, Li metal counter electrode, and electrolytes in a 2032-coin cell, and performed in a bath with a constant temperature of 25°C. The upper and the lower limits of the potential were 4.95 V to 2.6 V vs. Li/Li^+ , and the charge-discharge load was 0.1 C at a constant current.

As the electrolyte, 1.0 mol/L of LiPF_6 was dissolved in EC, EMC, and vinylene carbonate as a carbonate solvent at the volume ratio of 30:69:1 (hereafter referred to as carbonate electrolyte). We also created a prototype electrolyte comprising organic solvents for which enhancements of oxidative stability is anticipated.

4. Results and Discussions

4.1. The Relationship between η and Oxidation Potential

Calculation of E_{HOMO} and E_{LUMO} of organic solvents is shown in Fig. 4. Because η is calculated from E_{HOMO} and E_{LUMO} using Eq. (1), diagonal lines in Fig. 4 have the same value. The basic structure of carbonate solvent, EC and DMC, showed a tendency where the fluorinated alkyl group substitution of side chain R_1 to R_4 increased E_{HOMO} and decreased E_{LUMO} . However, there was no notable change from $\eta = 3.25$. This trend was consistent with the result of Yamaki et al.⁽²⁸⁾, where ΔE of the polar solvent was mostly

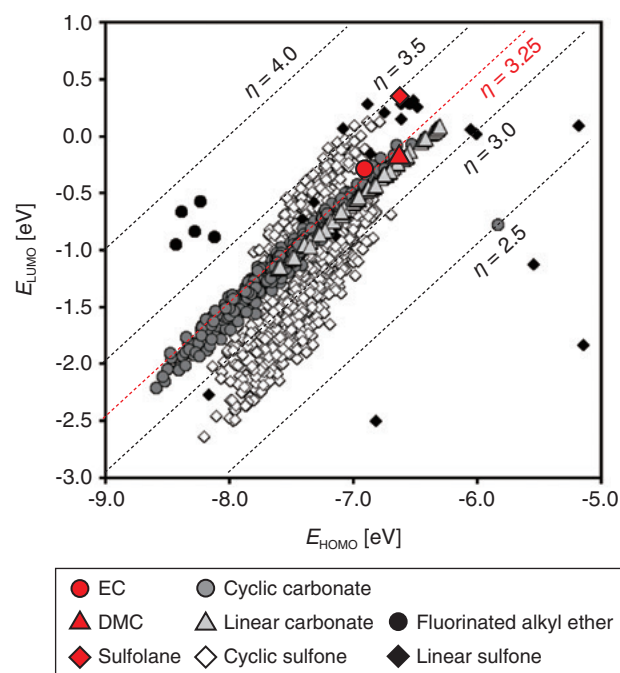


Fig. 4 HOMO and LUMO energy levels of various organic solvents

the same regardless of the type of solvent. Fluorinated alkyl ether and part of the cyclic sulfone and linear sulfone were the only basic structures where an increase of η was confirmed against carbonate solvents and their fluorinated alkyl group substitution. The molecular structure where the fluorinated alkyl group substitution of the side chain R_1 to R_8 was performed against the basic structure of cyclic sulfone, sulfolane, did not present a meaningful increase in η . In most substituted structures, η decreased.

Subsequently, among solvents that had DFT geometry optimization performed, we measured the oxidation potential with LSV in solvents that could be procured. Figure 5 shows the LSV measurement results. Oxidative current was confirmed from 4.8 V regardless of the molecular structure in the carbonate organic solvents [Fig. 5(a)]. The oxidative current of fluorinated alkyl ether (FAE1 to FAE3) was confirmed from around 5.5 V in the fluorine substitution solvents, indicating an enhancement of oxidative stability from the carbonate solvents by 0.7 V. The oxidative current of sulfolane was confirmed to be approximately 6 V in solvents that contain sulfur in the main chain [Fig. 5(c)], indicating an enhancement of oxidative stability from the carbonate solvents by 1.2 V. Figure 6 and Table 1 show the relationship between the oxidation potential and η of organic solvents estimated

from the above LSV measurement results. It indicated that the η and oxidation potential have a linear correlation. To enhance the oxidative stability of electrolytes, it would be

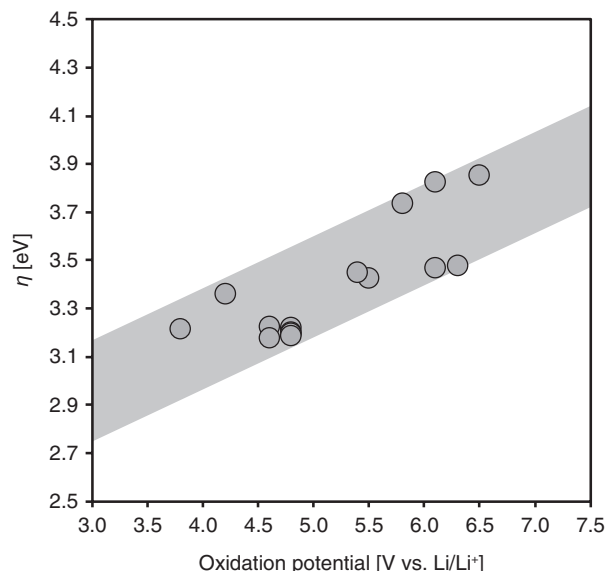


Fig. 6 Correlation between oxidation potential and η for several organic solvents

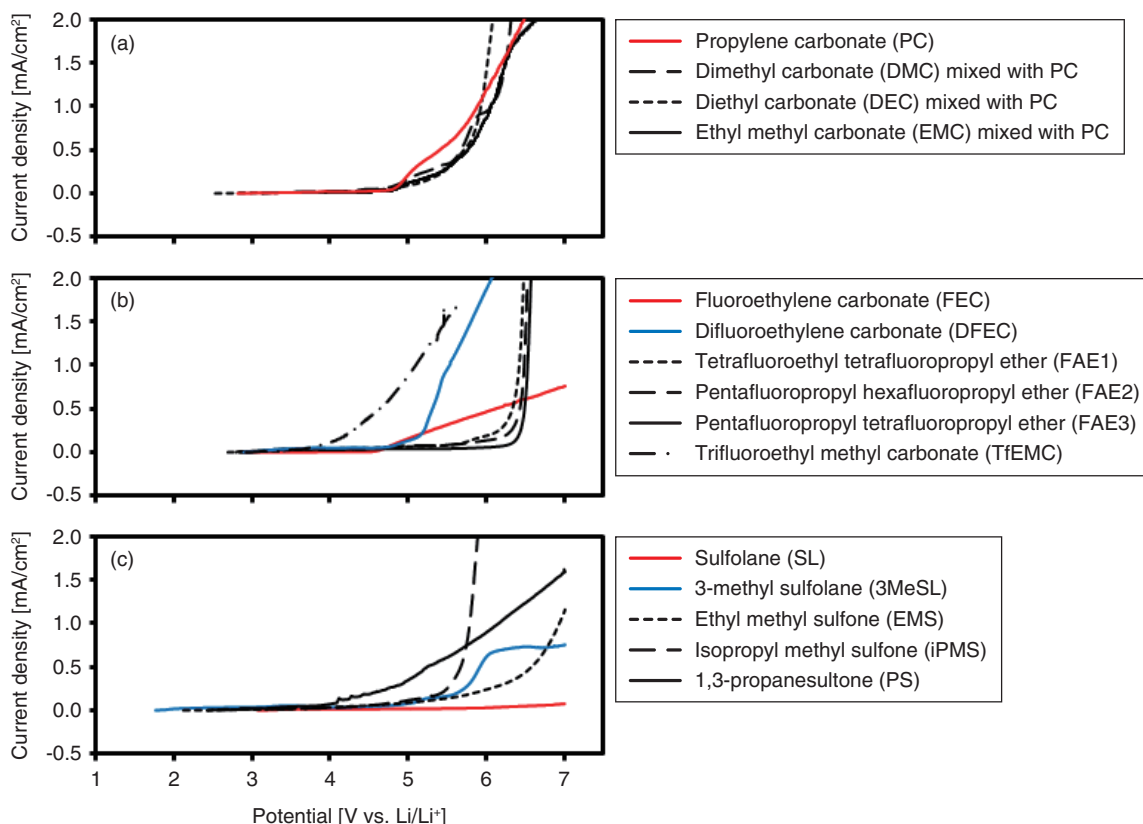


Fig. 5 LSV curves of (a) carbonate solvents, (b) fluorinate solvents, and (c) sulfonate solvents

Table 1 E_{HOMO} , E_{LUMO} , η , and oxidation potential of solvents

Solvent	E_{HOMO} [eV]	E_{LUMO} [eV]	η	Oxidation potential [V vs. Li/Li ⁺]
Propylene carbonate (PC)	-6.722	-0.279	3.222	4.8
Dimethyl carbonate (DMC)	-6.546	-0.143	3.201	4.8
Diethyl carbonate (DEC)	-6.367	0.010	3.189	4.8
Ethyl methyl carbonate (EMC)	-6.454	-0.063	3.196	4.8
Fluoroethylene carbonate (FEC)	-7.340	-0.885	3.228	4.6
Difluoroethylene carbonate (DFEC)	-7.747	-1.390	3.179	4.6
Tetrafluoroethyl tetrafluoropropyl ether (FAE1)	-8.233	-0.577	3.828	6.1
Pentafluoropropyl hexafluoropropyl ether (FAE2)	-8.426	-0.955	3.736	5.8
Pentafluoropropyl tetrafluoropropyl ether (FAE3)	-8.381	-0.672	3.855	6.5
Trifluoroethyl methyl carbonate (TFEMC)	-7.091	-0.655	3.218	3.8
Sulfolane (SL)	-6.603	0.333	3.468	6.1
3-methyl sulfolane (3MeSL)	-6.503	0.292	3.428	5.5
Ethyl methyl sulfone (EMS)	-6.750	0.210	3.480	6.3
Isopropyl methyl sulfone (iPMS)	-6.619	0.285	3.452	5.4
1,3-propanesultone (PS)	-6.867	-0.147	3.360	4.2

desirable to prepare electrolytes using solvent molecules with large η only.

4.2. Formulation of the Prototype Electrolyte and Confirmation of the Potential Window

Sulfolane (SL), a type of fluorinated alkyl ether, pentafluoropropyl tetrafluoropropyl ether (FAE3), and vinylene carbonate (VC) were mixed at the volume ratio of 30:69:1 respectively, as an organic solvent with enhanced oxidative stability. When LiPF₆ was dissolved in this mixed solvent, an insoluble component was confirmed at the concentration of 0.7 mol/L or more. Thus, we stirred and dissolved the LiPF₆ at 0.6 mol/L at room temperature as the prototype electrolyte. Given that SL and FAE3 had no known reports regarding reduction film formation on a Li metal anode, we used VC^{(29), (30)} as a general additive.

Figure 7 shows the LSV measurement result of the prototype electrolyte and cyclic voltammogram of the LNMO4 cathode. The result of oxidizing sweep showed that the oxidative current of the prototype electrolyte was confirmed from 6.0 V vs. Li/Li⁺. There was an enhancement of the oxidative stability of the carbonate solvents [Fig. 5(a)] by about 1.2 V vs. Li/Li⁺. Conversely, in the reducing sweep, there was a reducing current likely from the formation of a VC-reducing film near 1.0 V vs. Li/Li⁺ and because of Li metal precipitation at 0 V vs. Li/Li⁺. Consequently, the potential window of the prototype electrolyte was 0 V to 6.0 V vs. Li/Li⁺. Subsequently,

to confirm whether the oxidation/reduction reaction of LNMO4 can occur reversibly within the potential window of the prototype electrolyte, we performed a CV measurement. Figure 7 confirmed an oxidation peak of 4.9 V vs. Li/Li⁺, and a corresponding reduction peak of 4.5 V vs. Li/Li⁺. These oxidation and reduction peaks could be sufficiently covered by the potential window of the prototype electrolyte.

4.3. Confirmation of Enhancements of Oxidative Stability with a Cyclic Charge-discharge Test

Figure 8 shows the result of a cyclic charge-discharge test that used an LNMO4 cathode. The initial discharge capacity was 137 mAh/g for a cell that used the carbonate electrolytes (hereafter referred to as Cell_{conv}) and 134 mAh/g for a cell that used the prototype electrolyte (hereafter referred to as Cell_{proto}). These were 93% and 91% of the theoretical capacity of LNMO4 (147 mAh/g), respectively. When the number of cycles needed for the capacity to reach 80% relative to the initial discharge capacity was compared, it was found that the durability was increased to 45 cycles for the Cell_{conv} and 80 cycles for the Cell_{proto}. As for the Coulombic efficiency, it was about 99% for the Cell_{proto}, and decomposition reaction of the electrolyte was likely not to occur. However, a reduction in the Coulombic efficiency was confirmed in the Cell_{conv} after 32 cycles. After 54 cycles, the seal of the coin cell was opened, as shown in the Fig. 8, making it incapable of charging or discharging. In the LSV measurement result shown in Fig. 5(a), oxidation of the carbonate electrolytes was indicated from 4.8 V vs. Li/Li⁺, it is assumed that the gas emitted from oxidation of the carbonate electrolytes accumulated in the

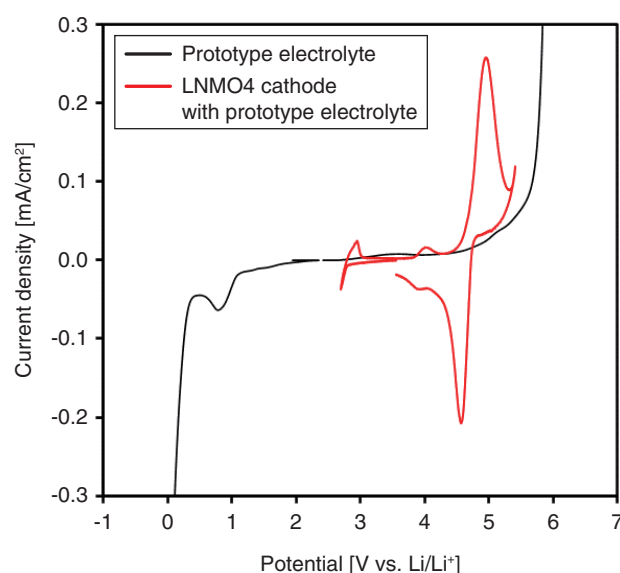


Fig. 7 LSV curve of prototype electrolyte and CV curve of LNMO4 cathode with prototype electrolyte

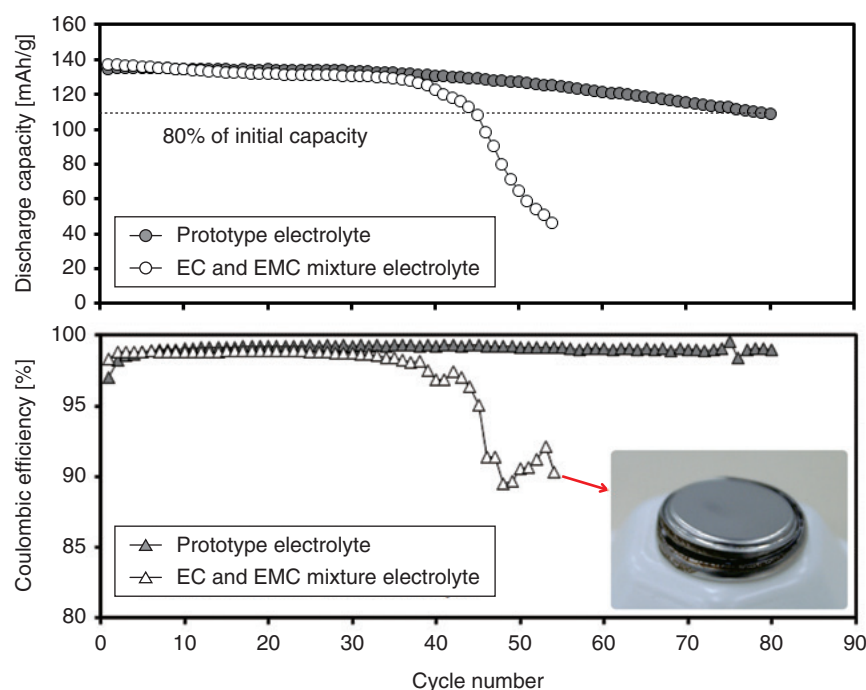


Fig. 8 Discharge capacity and coulombic efficiency vs. cycle number for LNMO4 - Li cell compared with different electrolyte composition

$\text{Cell}_{\text{conv}}$, and the increased pressure in the cell released the seal.

Consequently, enhancements in the oxidative stability of the prototype electrolyte, where the solvent was chosen by the relationship between η and the oxidation potential, were confirmed. We successfully extended the cycle life of LNMO4 by 1.7 times.

5. Conclusions

In response to high-voltage operation of lithium-ion rechargeable batteries, we examined enhancements of the oxidative stability of electrolytes. As an examination method, we applied a calculation index η that estimates the oxidation potential of organic solvents. We reached the following conclusions:

- (1) There was a linear correlation between the measured oxidation potential and η of organic solvents.
- (2) The prototype electrolyte that used sulfolane and fluorinated alkyl ether, for which an enhancement of oxidative stability has been achieved, presented the oxidative stability of 6.0 V vs. Li/Li^+ .
- (3) The use of the above prototype electrolyte extended the charge-discharge cycle life of LNMO4 by 1.7 times.

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Author



Yoshiyuki MORITA



Hiroto MAEYAMA



Atsushi FURUKAWA