Strategy for Cyclability Prolongation of Li$_3$V$_2$O$_4$/Li$_3$V$_2$(PO$_4$)$_3$ Full Cells Based on Charge-Discharge Cycling Simulation

Yu CHIKAOKA, a, b, c Reiko OKUDA, a Etsuro IWAMA, b, d, * Masafumi KUWAO, a Wako NAOI, c and Katsuhiko NAOI, d, *

a Department of Applied Chemistry, Tokyo University of Agriculture & Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8558, Japan
b Global Innovation Research Organization, Tokyo University of Agriculture & Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8558, Japan
c Division of Art and Innovative Technologies, K & W Inc., 1-3-16-901 Higashi, Kunitachi, Tokyo 186-0002, Japan
d Advanced Capacitor Research Center, Tokyo University of Agriculture & Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8558, Japan

* Corresponding authors: iwama@cc.tuat.ac.jp (E. I.), k-naoi@cc.tuat.ac.jp (K. N.)

ABSTRACT
Full cells employing Li$_3$V$_2$O$_4$ (LVO) and Li$_3$V$_2$(PO$_4$)$_3$ (LVP) as anode and cathode, respectively, are energy storage devices offering high power and cyclability. Such full cells, termed as LVO/LVP, were constructed in this study, and they exhibited low capacity retention (72%) over 1000 cycles at a high temperature of 50 °C. We clarified the capacity degradation mechanism using charge-discharge cycling simulations based on a difference in coulombic efficiency (CE) between two electrodes with/without a capacity decay at electrode materials. Simulation results indicate that the low CE of LVO accompanied with a cyclic capacity decay of LVO was responsible for the full cell capacity degradation. The LVO capacity decay was further elucidated by experimental evidences, showing that the cycled LVO was covered by resistive films derived from the electrolyte reductive decomposition. Indeed, the capacity retention of full cell cycling was improved to 86–96% by mitigating the effect of such side reaction, demonstrating the credibility and effectivity of our simple cycling simulation. Our finding may help to elucidate the degradation mode of the full cell cycling with less experimental efforts and work out own strategy to mitigate the degradation.

© The Author(s) 2020. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.20-00162].

Keywords : Li$_3$V$_2$O$_4$/Li$_3$V$_2$(PO$_4$)$_3$ Full Cell, N/P Capacity Ratio, Cyclability, Charge-discharge Simulation

1. Introduction
In response to the growing concerns over environmental problems, the demand for high-power electric energy storage (EES) devices for grid storage has been increasing to service a sustainable society. One of the examples as such high-power EES devices is an electric double-layer capacitor (EDLC) or supercapacitors (SC), which is also characterized by its safety and extremely long cycle life. However, the energy density and cell voltage of EDLCs are limited compared to those of batteries because of their charge-storage mechanism utilizing ionic adsorption on the surface of activated carbon (AC) electrodes. 1, 2 Hybrid/asymmetric capacitors as the 2nd generation (2nd gen.) SC have been proposed to improve the voltage and energy density of EDLC, which replace one of their AC electrodes with battery materials—in most cases lithium ion battery (LIB) materials—that exhibit high power and high cyclability. 3–5 To further achieve higher energy density than hybrid capacitors while maintaining high power and cyclability, however, it is inevitable to replace the remaining AC electrode with another battery material with ultrastraf electrochemical characteristics, i.e., to construct LIBs with capacitor-like characteristics, which we term SuperRedox Capacitors (SRC) as the 3rd gen. SC. 6 Depending on the combination of active materials, SRC may achieve different maximum cell voltages (2.8–3.5 V) and energy density (5.4–5.7 fold of EDLC).

One of the promising combinations of active materials for such SRCs is lithium vanadate (Li$_3$V$_2$O$_4$, LVO) anode//lithium vanadium phosphate (Li$_3$V$_2$(PO$_4$)$_3$, LVP) cathode. LVO has attracted significant attention as an anode material because of its lower reaction potentials and higher theoretical capacity compared to those of typical Ti-based anode materials such as Li$_4$Ti$_5$O$_12$ (LTO) (ca. 1.55 V vs. Li/Li¹) and 175 mAh g$^{-1}$). 7–9 The redox reactions of LVO ($V^{5+}$/$V^{3+}$) lies in a safe potential range from 0.4 to 1.3 V vs. Li/Li¹ and show the reversible lithiation/delithiation with the capacity of 197 mAh g$^{-1}$ (equivalent to 1.0 Li insertion) and 394 mAh g$^{-1}$ (equivalent to 2.0 Li insertion). 10, 11 LVP is a polyanionic cathode material characterized by strong PO$_4$ bonds that ensure excellent thermal stability compared to other common cathode materials such as LiCoO$_2$. 12 The inductive effect of such PO$_4$ increase the LVP reaction potential (3.6–4.1 V vs. Li/Li¹), where the insertion/
deinsertion of 2.0 Li with a theoretical capacity of 131 mAh g⁻¹ reversibly occurs.¹⁰⁻¹² Three dimensional Li⁺ diffusion in LVP gives a higher lithium-ion diffusion coefficient (10⁻¹⁰ cm² s⁻¹) compared to that of other polygon-type cathodes such as LiFePO₄ (10⁻¹³ cm² s⁻¹), respectively.¹²⁻¹⁴ Still, both LVO and LVP have inherent disadvantages to achieve high power capability; low electrical conductivity (LVO < 10⁻¹⁰ Ω⁻¹ cm⁻¹, LVP: 10⁻⁷⁻¹⁰⁻⁸ Ω⁻¹ cm⁻¹) and large charge-discharge potential hysteresis (LVO < 500 mV).⁶ To overcome such inherent disadvantages and enhance the power capability of LVO anodes and LVP cathodes, several approaches have been reported such as nanosizing (5–100 nm), carbon coating, and metal dopings.⁹⁻¹⁵⁻¹⁸ Previously, we successfully synthesized nanocomposites of LVO and LVP with multi-walled carbon nanotubes (MWCNTs) via our unique technique called ultra-centrifugation (uc) treatment, which enables the synthesis of oxide nanoparticles highly dispersed within nanocarbon matrix.⁸⁻¹² Both uc-treated LVO (uc-LVO) and uc-treated LVP (uc-LVP) showed excellent power capability (> 50 % of capacity retention even at a high current density of 20 A g⁻¹) high cyclability (90 % capacity retention of the initial cycle over 4000 cycles).⁸⁻¹² These materials enabled us to develop a high-power device termed as a uc-LVO/uc-LVP full cell (see Fig. S1 of the Supporting Information).

In a full cell composed of an LVP cathode, however, an important issue is the limitation of its cycling performance, as the small amount of eluted vanadium from the LVP can be deposited on the opposite anodic side and the deposited vanadium may catalytically accelerate the electrolyte reductive decomposition. In previous studies on the full cells composed of uc-LVP such as LTO/uc-LVP,⁹ the degradation mechanism of full cell capacity attributed to the eluted vanadium was elucidated by the direct detection of vanadium species on the LTO anode surface via inductively coupled plasma (ICP) and X-ray photoelectron spectroscopy (XPS). Similar degradation mechanism may be predicted for the uc-LVO/uc-LVP full cells, however, the detection of such vanadium species becomes much difficult when the anode composed of the vanadium-based materials same as the LVP. In this connection, we focus on the charge-discharge cycle simulation as an “indirect” analysis method, and an alternative to the direct detection of the vanadium species.

In this study, to elucidate the capacity degradation mechanism of uc-LVO/uc-LVP full cell cycling, we applied simple charge-discharge simulations based on a difference in coulombic efficiency (CE) between anode and cathode with/without a capacity decay at electrode materials. Prior to the simulation, we collected the experimental data of the full cell cycling at different values of negative and positive electrodes (anodes and cathodes) capacity ratio (N/P capacity ratio). Then, we performed different patterns of simulations and compared them with experimental data. Here, we simply focused on the direction of potential shifts in simulated charge-discharge curves. After successfully identifying the capacity decay of uc-LVO as a factor for the capacity degradation of full cells, additional experimental data such as scanning electron microscopy (SEM) observation were collected to support the assumption derived from the simulation. Furthermore, vinylene carbonate (VC) was chosen as an electrolyte additive to mitigate the capacity decay of uc-LVO by facilitating the formation of a stable film on the uc-LVO anode, demonstrating the credibility and effectivity of our simple cycling simulation. Our finding may help to efficiently elucidate the degradation mode of the full cell cycling and work out own strategy to mitigate it.

2. Experimental

2.1 Materials

NH₄VO₃ (99 %, Kanto Chemicals Co.), citric acid (99.5 %, Sigma-Aldrich Co.), ethylene glycol (99 %, FUJIFILM Wako Pure Chemical Co.), and lithium hydroxide (98 %, Kishida Chemical Co.) were used to prepare the uc-LVO anode.⁸ NH₄VO₃ (99 %, Kanto Chemicals Co.), CH₃COOLi (98.0 %, FUJIFILM Wako Pure Chemical Co.), H₂PO₄ (85.0 %, FUJIFILM Wako Pure Chemical Co.), citric acid (99.5 %, Sigma-Aldrich Co.), and ethylene glycol (99 %, FUJIFILM Wako Pure Chemical Co.) were used to prepare uc-LVP cathode.¹² Multi-walled carbon nanotubes (MWCNTs), which have a specific surface area of 240 m² g⁻¹, were provided by Ube Industries.

2.2 Electrode preparation

The uc-LVO/MWCNTs (60:40 wt%) to be used as the anode and the uc-LVP/MWCNTs (70:30 wt%) to be used as the cathode were prepared using the method developed in our previous studies.⁸⁻¹² We verified that both active materials were synthesized based on their diffraction peaks, carbon weight, and electrochemical properties by using X-ray diffraction, thermogravimetric analysis, and charge-discharge tests in half-cells, respectively (Figs. S2 and S3). The uc-LVO/MWCNTs anodes were prepared by mixing 94 wt% of the sample and 6 wt% of polyvinylidene difluoride (PVDF, Kureha Industries) in n-methyl pyrrolidone (NMP, FUJIFILM Wako Pure Chemical Co.) and then coating it on etched-Cu foil. The uc-LVP/MWCNTs cathodes were prepared by mixing 90 wt% of the composite and 10 wt% of PVDF in NMP and then coating it on etched-Al foil. Both coated electrodes were dried at 80 °C under vacuum for 12 h. Prior to cell assembly, the electrodes were further dried at 80 °C for 3 h under vacuum. Three different loading masses of the uc-LVO anode were used to control the N/P capacity ratios. The uc-LVO/MWCNTs loading masses used for the full cells with N/P capacity ratios of 1.1, 1.4, and 1.8 were ca. 0.65, 0.80, and 1.1 mg cm⁻² with thicknesses of ca. 12, 16, and 22 µm, respectively. The uc-LVP/MWCNTs loading mass was approximately 1.15 mg cm⁻² with a thickness of 15 µm. The variations in cell potentials with respect to the N/P capacity ratio are described in Section 2.4.

2.3 Cell assembly

The uc-LVO//uc-LVP full cells were assembled using the uc-LVO anode and uc-LVP cathode in laminate-type cells with a Li metal reference electrode. The electrode areas of the half-cells (coin-type) and full cells (laminated-type) were 1.54 and 5.0 cm², respectively. The electrolyte was a mixture of EC: DEC (1:1 vol%) containing 1.0 mol L⁻¹ LiPF₆ (battery grade, Kishida Chemical Co.) with or without 5 wt% VC (battery grade, Kishida Chemical Co.), and the separator was a 25 µm-thick monolayer polypropylene separator (Celgard2400, Celgard Co.). Prior to full cell cycling, electrochemical pre-conditioning (including Li⁺ pre-doping) of the uc-LVO anode and uc-LVP cathode was conducted through initial charge-discharge cycling. Details of the abovementioned process are presented in the Supporting Information (see the section entitled “Pre-conditioning procedure of uc-LVO anode and uc-LVP cathode”). The cell capacity for uc-LVO//uc-LVP full cells was LVP-limited, corresponding to 74 mAh g⁻¹ per uc-LVP composite (1 C-rate = 74 mA g⁻¹ per uc-LVP composite). The 2032 coin-type half-cells (Li//uc-LVO and Li//uc-LVP) were assembled to check the exhibited capacity of active materials. Both laminated and coin-type cells were assembled in a dry room (dew-point temperature < –40 °C).

2.4 Charge-discharge conditions

The charge-discharge conditions in uc-LVO//uc-LVP full cells vary with respect to the N/P capacity ratios, as shown in Fig. 1. Here, we defined the N/P = 1 when the potential ranges of uc-LVO and uc-LVP lied within 0.6–2.5 V and 3.35–4.1 V vs. Li/Li⁺, respectively. It should be noted that the potential of uc-LVO (2.5–0.6 V vs. Li/Li⁺), which corresponds to 1.5-electron reactions
Figure 1. (a) Potential curves of uc-LVO and uc-LVP in uc-LVO//uc-LVP full cell configurations at N/P capacity ratios of 1.1, 1.4, and 1.8. (b) Potential curves of uc-LVO and uc-LVP at N/P = 1.1 uc-LVO//uc-LVP full cell. [Inset table] LVO MinV is the lowest potential of the uc-LVO charge curve (C: N/P = 1.1, △: N/P = 1.4, and □: N/P = 1.8), and Cell V corresponds to the potential difference between the uc-LVO and uc-LVP in the uc-LVO//uc-LVP full cells at different N/P capacity ratio (1.90–3.50 V: N/P = 1.1, 2.05–3.50 V: N/P = 1.4, 2.25–3.50 V: N/P = 1.8).

(145 mAh g⁻¹), was determined to reduce the effect of charge-discharge hysteresis (from 100 to 250 mV), which gradually increases between the two-electron reaction (0.76–10 V vs. Li/Li⁺) and the one-electron reaction (2.5–0.76 V vs. Li/Li⁺). In these potential regions, the reaction of uc-LVO can be described as follows:21

\[
\text{Li}_2\text{VO}_4 + 1.5 \text{Li}^+ + 1.5 e^- \rightleftharpoons \text{Li}_4(\text{Li},\text{V})\text{O}_4
\]  

(1)

The potential of the uc-LVP cathode (3.35–4.1 V vs. Li/Li⁺) with 74 mAh g⁻¹ (per uc-LVP composite) was determined to prevent the three-electron reaction (approximately over 4.5 V vs. Li/Li⁺), which causes LVP degradation during full cell operation.21,22 For uc-LVP, three-step plateau regions should be observed for the 0.5 Li⁺ (3.60 V), 1.0 Li⁺ (3.65 V), and 2.0 Li⁺ (4.05 V) reactions, corresponding to Eqs. (2)–(4), respectively, as follow:21

\[
\begin{align*}
\text{Li}_2\text{V}_2(\text{PO}_4)_3 + 0.5 \text{Li}^+ + 0.5 e^- & \rightleftharpoons \text{Li}_2\text{V}_2(\text{PO}_4)_3 \\
\text{Li}_2\text{V}_2(\text{PO}_4)_3 + 0.5 \text{Li}^+ + 0.5 e^- & \rightleftharpoons \text{Li}_2\text{V}_2(\text{PO}_4)_3 \\
\text{Li}_2\text{V}_2(\text{PO}_4)_3 + \text{Li}^+ + e^- & \rightleftharpoons \text{Li}_2\text{V}_2(\text{PO}_4)_3
\end{align*}
\]

(2–4)

By changing N/P capacity ratios to 1.1, 1.4, and 1.8, the lower voltages varied as 1.90, 2.05, and 2.25 V, respectively, whereas upper voltages of the uc-LVO//uc-LVP full cell remained at 3.5 V. Accordingly, only the uc-LVO upper limit potential (LVO MaxV) varied with different N/P capacity ratio as shown in the inset table of Fig. 1a. The example of potential curves at N/P = 1.1 is shown in Fig. 1b.

2.5 Simulation of charge-discharge behavior of uc-LVO//uc-LVP full cells

Simulations of charge-discharge profiles of uc-LVO//uc-LVP full cell were conducted to investigate the effect of N/P capacity ratio on the potential shifts of uc-LVO anode and uc-LVP cathode during cycling. Six different degradation patterns were simulated; first, simulated degradation conditions of charge-discharge curves were categorized in two patterns with discrepancy of coulombic efficiency (CE) between uc-LVO anode and uc-LVP cathode; i) \(CE_{\text{LVO}} > CE_{\text{LVP}}\) or ii) \(CE_{\text{LVO}} < CE_{\text{LVP}}\). The shift of potential curves of uc-LVO and uc-LVP during cycling depends on their CE magnitude relation whether i) or ii), as described in the Supporting Information section “Concept of charge-discharge simulation” and Fig. S4. Each of two i) and ii) patterns were further categorized into three patterns (six patterns in total) whether the degradation is accompanied with the capacity decay of electrodes; a) no capacity fade for both anode and cathode, i.e., the capacity of the full cells decreases purely due to the difference in CE, b) capacity decay for the LVP cathode, and c) capacity decay for the LVO anode.

In advance of the cycling simulation, we simplified the potential curves of uc-LVO anode and uc-LVP cathode in order to decrease cost of simulation; charge potential curves of the uc-LVO anode and the uc-LVP cathode obtained for Li metal half-cells were divided into 9 and 11 approximated lines, respectively (see Fig. S5). Note that, for the simplification, we also assumed that the discharge potential curves are identical of charge curves and disregarded the effect of internal resistance and potential hysteresis on the potential curves. As the potential curves in the simulation are composed of approximated lines, capacity decrease in total can be expressed by the change of their slopes. Thus, if we should only consider the CE difference between anode and cathode without any capacity decay of electrodes, the slope of the discharge potential profiles (\(S_{\text{Dis}}\)) can be expressed as follow:

\[
S_{\text{Dis}} = S_{\text{Cha}}/CE
\]  

(5)

where \(S_{\text{Cha}}\) is the slope of the charge curve. Based on the Eq. (5), the cycling simulations with Python code were conducted (see the section in Supporting Information “Simulation program for the uc-LVO//uc-LVP full cell charge-discharge cycling”). The used operating potentials of uc-LVO anode and uc-LVP cathode for various N/P capacity ratios are as described in the inset table of Fig. 1. In case that the degradation mode is accompanied with capacity decay of electrodes, the change in the slope of charge potential (\(S'_{\text{Cha,a}}\)) and discharge potential curves (\(S'_{\text{Dis,a}}\)) at the designated cycle number of uc-LVO//uc-LVP full cells (\(n\)) can be expressed as follows:

\[
S'_{\text{Cha,a}} = S_{\text{Cha}}/(F_{\text{dec}})^{n-1}
\]  

(6)

\[
S'_{\text{Dis,a}} = S_{\text{Dis}}/(F_{\text{dec}})^{n}
\]  

(7)

where \(F_{\text{dec}}\) is the capacity decay factor in which the exhibited capacity of the electrode decreases in proportion to the \(F_{\text{dec}}\) through cycle by cycle.

2.6 Surface analysis of uc-LVO//uc-LVP full cells

We observed the surface morphology of the uc-LVO and uc-LVP
Figure 2. (a–c) Charge-discharge curves of uc-LVO//uc-LVP full cells at 50 °C for 1st, 100th, 500th, and 1000th cycles at 0.74 A g⁻¹ (per uc-LVP composite, ca. 10 C-rate). (d) Capacity retention plots in uc-LVO//uc-LVP full cells. (e–g) Charge-discharge potential curves of individual uc-LVP and uc-LVO at 1st and 1000th cycles. Corresponding N/P capacity ratios are N/P = 1.1 for (a, e), 1.4 for (b, f), and 1.8 for (c, g), respectively.

3. Results and Discussion

3.1 Cyclability of uc-LVO//uc-LVP full cells with various N/P capacity ratios

The capacity ratio of the negative (anode) and positive (cathode), i.e., N/P capacity ratio of the cell, is an important factor for their cycle life, especially when the electrode active materials such as uc-LVO and uc-LVP show long cyclability (> 90% over 4000 cycles, see Fig. S3). Charge-discharge curves for the uc-LVO//uc-LVP full cells with three different N/P capacity ratios (1.1, 1.4, and 1.8) up to the 1000th cycle are shown in Figs. 2a–2c. Note that all the cyclability tests shown in Fig. 2 were conducted at 50 °C in order to accelerate the capacity degradation of uc-LVO//uc-LVP cells, whose capacity retention at room temperature (25 °C) did not show any degradation and difference among three N/P capacity ratio over 1000 cycles (> 95%, see Fig. S6). As shown in Fig. 2, at the 1st cycle, all the uc-LVO//uc-LVP cells show similar overall shape of charge-discharge curves with the capacity of about 70 mAh g⁻¹ (per uc-LVP composite) which typically reflects the combined characteristics of charge-discharge profiles of two electrodes; the slope of uc-LVO (see Fig. S5a) and inflection points at approximately 3.60, 3.65, and 4.05 V vs. Li/Li⁺ due to the three-step plateau of uc-LVP (see Fig. S5b). With an increase of cycle numbers, however, the difference among three cells became obvious. Charge-discharge curves for the uc-LVO//uc-LVP cell with N/P = 1.1 became distorted to reach the cut-off voltage of the full cell (1.9–3.5 V) earlier than at the 1st cycle, resulting in low capacity retention of 72% (decreased from 68 to 49 mAh g⁻¹). By increasing N/P capacity ratios (N/P = 1.4 and 1.8), the shapes of charge-discharge curves after 1000th cycle are less distorted, resulting in better capacity retention compared to that of N/P = 1.1. The capacity retention of the full cells increases with the N/P capacity ratio (N/P = 1.1, 72%; N/P = 1.4, 85%; and N/P = 1.8, 96%), as shown in Fig. 2d. Considering the excellent cyclability of the uc-LVO and uc-LVP themselves (Fig. S3), other than the degradation of active materials themselves may be responsible for the capacity degradation for uc-LVO//uc-LVP full cells.

Potential curves versus lithium reference electrode of uc-LVO anode and uc-LVP cathode during uc-LVO//uc-LVP full cell cycling are shown in Figs. 2e–2g. In the uc-LVP charge-discharge profile at N/P = 1.1 (Fig. 2c, upper portion), the first plateau region (0.5 Li⁺) at ca. 3.60 V vs. Li/Li⁺ disappeared and the length of second plateau region (1.0 Li⁺) at ca. 3.65 V vs. Li/Li⁺ shortened to 65% of the 1st cycle after 1000 cycles. Consequently, the termination potential of the uc-LVP discharge curve (LVP MinV') increased from 3.46 to 3.61 V vs. Li/Li⁺ (by 0.15 V) after 1000 cycles, whereas the LVP MaxV' remained almost the same (only changed from 4.14 to 4.15 V). The LVO MaxV and MinV' correspond to those of uc-LVP cathode; namely, the LVO MaxV' changed from 1.51 V to 1.66 V while the LVO MinV' remained almost the same. By increasing N/P capacity ratio over 1.4, the second plateau of uc-LVP cathode were retained after 1000 cycles and the length of the remaining first plateau became longer (60% and 85% at N/P = 1.4 and 1.8, respectively). Consequently, the shift of LVP MinV' and LVO MaxV' after 1000 cycles became smaller; 0.10 V and 0.06 V at N/P = 1.4 and 1.8, respectively. To give a reasonable explanation for such potential shift changes with different N/P capacity ratios during cycling, we analyzed the degradation behavior of the anodes and electrodes before and after cycling in the uc-LVO//uc-LVP full cell by using scanning electron microscopy (SEM; Hitachi model S5500) and XPS (JEOL Ltd., JPS-9200). Prior to the SEM and XPS measurements, the cycled electrodes were rinsed with dimethyl carbonate and dried overnight under vacuum. All samples were prepared in a glove box to minimize any possible contamination, and XPS was performed using AlKα (hn = 1486.6 eV) radiation under ultra-high vacuum. The XPS spectra were collected at a voltage of 12 kV and emission current of 10 mA. All XPS spectra were energy calibrated to the hydrocarbon peak with a binding energy of 284.8 eV.

Electrochemistry, 89(2), 204–210 (2021)
cathodes by simulating the charge-discharge curves of uc-LVO/uc-LVP full cells.

3.2 Charge-discharge simulation of uc-LVO/uc-LVP full cells

Simulations of charge-discharge profiles of uc-LVO/uc-LVP full cell were conducted to investigate the effect of N/P capacity ratio on the potential shifts of uc-LVO anode and uc-LVP cathode during cycling (section 3.1). Figure 3 presents the experimental result (potential curves) of uc-LVO anode and uc-LVP cathode during full cell cycling at N/P = 1.1 (Fig. 3a, reproduced Fig. 2e) and the results of six simulated degradation patterns (Figs. 3b–3g). For the reduction in calculation cost, the cycle number of simulations are limited to 50 by adjusting the values of CE and Fdec. Arrows in each figure indicate the direction of the potential shift after cycling, e.g., for the experimental data at N/P = 1.1 (Fig. 3a), LVO MinV and LVP MaxV remained constant (green arrows), while the LVO MaxV and LVP MinV shifted to higher potentials (red arrows). By focusing on such direction of arrows, one can easily identify which factors are responsible for the capacity degradation during the uc-LVO/uc-LVP full cell cycling. Among the six simulated conditions, there is only one condition, CE_{uc-LVO} < CE_{uc-LVP} with capacity decay of uc-LVO (Fig. 3g), which shows exactly the same direction of arrows observed in the experimental result (Fig. 3a). The obtained results suggest that the decrease in the LVO coulombic efficiency with capacity decay is responsible for the observed uc-LVO/uc-LVP full cell degradation. Using the derived condition, another simulation results with different three N/P capacity ratio (= 1.1, 1.4, and 1.8) were conducted; the potential shifts of simulated potential curves of uc-LVO and uc-LVP were consistent with the experimental curves (see Fig. S7). To support the simulated results, we checked charge-discharge characteristics of the cycled uc-LVO anode and uc-LVP cathode separately by dis-assembling the full cells after 1000 cycles and re-assembling the two Li metal half-cells (see Fig. S8). Re-assembled Li//uc-LVO half-cells exhibited only 76% of capacity retention of the value before full cell cycling, while no degradation were observed for Li//uc-LVP half-cells. The capacity recovery of the Li//uc-LVO by decreasing the current density by 10 fold (from 300 to 30 mA g\(^{-1}\) per uc-LVO composite) indicates that the capacity decay of uc-LVO after full cell cycling may be mainly due to the resistance increase of uc-LVO reaction. In fact, SEM images of the cycled uc-LVO anode in the uc-LVO//uc-LVP full cell configuration show the degraded uc-LVO anode covered with a polymeric film (Figs. S9a and S9b), while there was no significant difference for the uc-LVP surface before and after the full cell cycling. Such polymeric film formation, which may be derived from the electrolyte solvent decomposition, is considered to be responsible for the resistance increase of LVO reaction. The electrolyte decomposition at the uc-LVO surface may be caused by the deposited catalytic vanadium species on the LVO anode, which were originally diffused from uc-LVP cathode after dissolution as reported in the previous report for the LTO//uc-LVP full cells.\(^{19}\) The amount of such eluted vanadium species should be a very small quantity, indicated by the negligible capacity decay for re-assembled Li//uc-LVP half-cells (Fig. S8). In fact, in the previous report for the LTO//uc-LVP full cells,\(^{19}\) the percentage of eluted vanadium species over entire LVP was around 0.2 wt% (0.8 µg over 4.5 mg evaluated by ICP measurements) after 1000 cycles, where similar results (no detectable capacity degradation) were obtained for the re-assembled Li//uc-LVP full cells.

Considering the cycling simulation results and events occurring on the uc-LVO, the degradation mechanism of uc-LVO//uc-LVP full cells are considered to proceed as following (Fig. 4): (I) During the charge process, aside from the lithiation of uc-LVO, the reductive decomposition of the electrolyte on the uc-LVO anode surfaces leads to the formation of resistive polymeric surface films. (II) Consequently, the slope of the potential profiles in uc-LVO discharge curve became steeper due to its resistance increase. (III) The steeper uc-LVO discharge curve reaches to the discharge cut-off
Figure 4. Schematic of capacity degradation model in uc-LVO//uc-LVP full cells.

Voltage at higher potential than the one at the previous cycle, resulting in an increase of LVO Max\text{V} and LVP Min\text{V}. Then, as soon as the LVP Min\text{V} gets to the potential of the first plateau region of uc-LVP, the discharge capacity of the uc-LVO//uc-LVP full cell immediately decreases due to the state-of-charge shift of uc-LVP cathode. (IV) During the re-charge, the lost capacity during the discharge never recovers as the LVO Min\text{V} and LVP Max\text{V} remain almost unchanged compared to those of the previous charge process. The repetition of (II), (III), and (IV) continuously cause a shift of LVO Max\text{V} and LVP Min\text{V} towards higher values, and the first and second plateaus of uc-LVP became shorter, leading to a pronounced capacity loss. As the N/P capacity ratio increased, the influence of resistance increase of uc-LVO anode reaction was mitigated because the slope of uc-LVP potential curves became gentle, resulting in the suppression of the increase of LVO Max\text{V} and LVP Min\text{V} and thus capacity decay.

3.3 Suppression of capacity decays of the uc-LVO anode using VC additives

As discussed in Sections 3.1 and 3.2, a high N/P system in uc-LVO//uc-LVP full cells reduced an impact of resistance increase of uc-LVO reaction on the potential shifts of LVO Max\text{V} and LVP Min\text{V} and thus improves the capacity retention of uc-LVO//uc-LVP full cells. A high N/P (1.4 and 1.8) system, however, unavoidably sacrifices its specific capacity and thus energy density. Accordingly, it is ideal to assemble the full cell with N/P capacity ratio as close as possible to 1. As the N/P capacity ratio increases, the excess uc-LVO capacity increases, and the calculated energy density per gram of composite (uc-LVP cathode + uc-LVO anode) is 135, 125, and 120 Wh kg\(^{-1}\) at N/P capacity ratios of 1.1, 1.4, and 1.8, respectively. For designing a full cell with a low N/P capacity ratio, it is important to suppress electrolyte decomposition at the uc-LVO anode, which leads to the formation of a resistive polymeric film on the uc-LVO surface (see Fig. S9). Here, an improvement in the cyclability of uc-LVO//uc-LVP full cells at low N/P capacity ratio (= 1.1), to be more precise, the suppression of the electrolyte decomposition on the uc-LVO anode was achieved by adding a VC in the electrolyte. VC was chosen as an additive to form the protective layer, which has been widely applied for other anode materials such as graphite and Si.\(^{24-29}\) As shown in the differential capacity (dQ/dV) plots of the Li//uc-LVO half-cell (see Fig. S10) with and without addition of VC, the reductive peak for the electrolyte with VC was observed at higher potential (0.74 V vs. Li/Li\(^+\)) compared to that without VC (0.70 V vs. Li/Li\(^+\)), indicating that the electrolyte reductive decomposition on the uc-LVO anode surface may be different in the presence of VC. The C1s and O1s XPS spectra for the uc-LVO surface after pre-conditioning (Figs. S11a and S11b) also indicate the different nature of decomposed products with and without the addition of VC, as the intensity of the peak around 287 eV (C1s, Fig. S11a) and around 533 eV (O1s, Fig. S11b) attributed to the C-O-C bonding increased while the peak around 290 eV in C1s attributed to the CO\(_2\) slightly diminished. Figure 5 depicts the characteristics of cycle performances for the uc-LVO//uc-LVP full cells using the VC-added electrolyte at a low N/P capacity ratio (N/P = 1.1) up to 1000 cycles at 50 °C. As shown in Fig. 5a, the charge-discharge curves for these cells showed a slight decrease of exhibited capacity (86% of capacity for the initial cycle), while maintaining overall curves shapes compared to the deformed curves without addition of VC (Fig. 2a). The potential curves of uc-LVP and uc-LVO for the full cells tested with VC (Fig. 5b) show that the shift of LVP Min\text{V} and LVO Max\text{V} after 1000 cycles were mitigated as 0.08 V compared to that for the cells without VC (0.15 V). Accordingly, the second plateau region (1.0 Li\(^+\) reaction) of uc-LVP were maintained even after 1000 cycles, similar to the case of using a high N/P capacity ratio without the VC additive. As shown in Fig. S12, the direct current internal resistance (DCIR) of uc-LVO//uc-LVP after the initial three cycles is higher with VC (9.9 m\(\Omega\)) than that without VC (8.8 m\(\Omega\)), which can be due to the formation of passivation film derived from decomposed VC on the LVO surface. After 1000 cycles, however, the DCIR with VC (14.7 m\(\Omega\)) became lower than that without VC (17.4 m\(\Omega\)). These results suggest that the VC-derived passivate film formed on the uc-LVO anode during pre-conditioning may effectively suppress the electrolyte decomposition (Figs. S9c and S9f) and thus improve the CE of uc-LVO anode, leading to the mitigation of the potential shifts of LVP Min\text{V} and LVO Max\text{V}. As shown in Fig. 5c, the capacity retention at N/P = 1.1 improved from 72 to 86% on employing VC, which is comparable with those obtained with higher N/P capacity ratios (>1.4). These results demonstrate that our simple cycling simulation may help to find out the degradation mode of the full cell cycling with less experimental efforts and work out own strategy to mitigate the capacity degradation.

4. Conclusions

In conclusion, to elucidate the capacity degradation mechanism of full cells, the simple cycling simulation method was applied and verified as an “indirect” method to predict the degradation factors without need for any dis-assembling of the cells. First, we evaluated the cyclability of uc-LVO//uc-LVP full cells at 50 °C under varying N/P capacity ratios, and observed the accelerated capacity degradation for the cells at low N/P = 1.1 (capacity retention = 72% after the 1000th cycle) compared to those at higher N/P ≥ 1.4 (85–96%). Then, the cycling simulation based on the CE and \(F_{\text{disc}}\) of the anode and cathode was applied to see the potential shifts of uc-
LVO and uc-LVP. By focusing on such potential shifts during cycling, we successfully found out that the capacity decay of uc-LVO anode was a factor promoting the capacity degradation of uc-LVO//uc-LVP full cells especially at low N/P = 1.1. SEM observation and a decrease in the exhibited capacity of cycled uc-LVO anode support the obtained simulation results, and also indicate that such capacity decay of uc-LVO anode was caused by an increase in its resistance due to the electrolyte decomposition at the uc-LVO anode. The cyclability improvement of full cells at N = 1.1 by adding 5 wt% of VC in the electrolyte demonstrated that the passivation of uc-LVO anode with the VC-derived film was effective to prevent the electrolyte decomposition at uc-LVO anode and thus to mitigate the capacity decay of uc-LVO, showing the credibility of prediction through our simple simulation method. Although further verification are certainly required, we believe that the application of our simple simulation can be extended to other full cell systems with a combination of any kinds of electrode materials and electrolyte compositions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, etc.), and may aid to reduce the cost of time and resources for the related research topics.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00162.

Acknowledgments

This study was supported by the Global Innovation Research Organization in TUAT. This study was supported by JSPS Grant-in-Aid for Scientific Research (KAKENHI) A under Grant No. JP19H00882, and the Center of Innovation Program from Japan Science and Technology Agency (A-STEP; AS282S002d).

References

1. M. Endo, T. Takeda, Y. Kim, K. Koshiba, and K. Ishii, Carbon letters, 1, 117 (2001).
2. B. Fang and L. Binder, J. Phys. Chem. B, 110, 7877 (2006).
3. K. Naio, Fuel Cells, 10, 825 (2010).
4. V. Augustyn, P. Simon, and B. Dunn, Energy Environ. Sci., 7, 1597 (2014).
5. G. G. Amatucci, F. Badway, A. Du Pasquier, and T. Zheng, J. Electrochem. Soc., 148, A930 (2001).
6. N. Okita, E. Iwama, and K. Naio, Electrochemistry, 88, 83 (2020).
7. H. Li, X. Liu, T. Zhai, D. Li, and H. Zhou, Adv Energy Mater., 3, 428 (2013).
8. E. Iwama, N. Kawabata, N. Nishio, K. Kisui, J. Miyamoto, W. Naio, P. Rozier, P. Simon, and K. Naio, ACS Nano, 10, 5398 (2016).
9. L. Shen, S. Chen, J. Maier, and Y. Yu, Adv. Mater., 29, 1701571 (2017).
10. K. Zhao, J. Tu, X. Wang, D. Zhang, J. Xiang, Y. Mai, and C. Gu, J. Power Sources, 196, 7715 (2011).
11. N. Membreho, K. Park, B. Goodenough, and K. J. Stevenson, Chem. Mater., 27, 3332 (2015).
12. K. Naio, K. Kisui, E. Iwama, Y. Sato, M. Shinoda, N. Okita, and W. Naio, J. Electrochem. Soc., 162, A827 (2015).
13. M. Saedi, J. Barker, H. Huang, J. Swoyer, and G. Adanson, Electrochem. Solid-State Lett., 5, A149 (2002).
14. A. Yamada, S-C. Chung, and K. Hinokuma, J. Electrochem. Soc., 148, A224 (2001).
15. X. Wang, B. Qin, D. Sui, Z. Sun, Y. Zhou, H. Zhang, and Y. Chen, Energy Technol., 6, 2074 (2018).
16. X. Rui, D. Sim, K. Wong, J. Zhu, W. Liu, C. Xu, H. Tan, N. Xiao, H. H. Hing, and T. M. Lim, J. Power Sources, 214, 171 (2012).
17. L. Zhang, H. Xiang, Z. Li, and H. Wang, J. Power Sources, 203, 121 (2012).
18. C. Wang, W. Shen, and H. Liu, New J. Chem., 38, 430 (2014).
19. N. Okita, E. Iwama, S. Tatsumi, T. H. Vo, W. Naio, M. T. H. Reid, and K. Naio, Electrochemistry, 87, 148 (2019).
20. B. Akekin, M. J. Lacev, T. Nordh, R. Younesi, C. Tengstedt, W. Zipprich, D. Brandell, and K. Edström, J. Phys. Chem. C, 122, 11234 (2018).
21. C. R. Birkl, M. R. Roberts, E. McTurk, P. G. Bruce, and D. A. Howey, J. Power Sources, 341, 373 (2017).
22. L. Wang, J. Xu, C. Wang, X. Cui, J. Li, and Y.-N. Zhou, RSC Adv., 5, 71684 (2015).
23. S-C. Yin, H. Grondy, P. Strobel, M. Anne, and L. F. Nazar, J. Am. Chem. Soc., 125, 10402 (2003).
24. L. Chen, K. Wang, X. Xie, and J. Xie, J. Power Sources, 174, 538 (2007).
25. E. Ouattara, R. Dheyivre, S. Siret, P. Bienss, S. Reynaud, P. Iratxabal, and D. Gonbeau, J. Electrochem. Soc., 156, A103 (2009).
26. H. Ota, Y. Sakata, A. Inoue, and S. Yamaguchi, J. Electrochem. Soc., 151, A1659 (2004).

Figure 5. Results of uc-LVO//uc-LVP full cell cycle test at N/P capacity ratio = 1.1 with an addition of 5 wt% of VC. (a) Charge-discharge curves cycled at 50 °C for 1st, 100th, 500th, and 1000th cycles at 0.74 A g⁻¹ (per uc-LVP composite, ca. 10 C-rate); (b) charge-discharge potential curves of uc-LVP and uc-LVO for 1st and 1000th cycles; and (c) capacity retention plots with or without VC additive.