



# Electrically conductive metal oxide-Assisted multifunctional separator for highly stable Lithium-Metal batteries

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## ARTICLE INFO

### Keywords:

Li-metal batteries  
Functionalized separator  
Niobium oxide  
Li ion redistribution  
Enhanced electrical conductivity

## ABSTRACT

Lithium (Li) metal anodes have received intensive attention owing to its high specific capacity and low redox potential. However, chronic issues related to dendritic Li growth have hindered the pragmatic use of Li-metal batteries (LMBs). As one of feasible approaches, depositing a functional material on the separator is an efficient strategy for improving the electrochemical stability of LMBs. In this paper, we report a functionalized separator, comprising a nitrated niobium dioxide (named as n-NbO<sub>2</sub>) and a polypropylene (PP) separator. It is identified that niobium oxide interact with metallic Li, resulting in redistributing the localized Li ion. The n-NbO<sub>2</sub>-coated separator with enhanced electrical conductivity promotes Li plating/stripping process, reinforcing the Li ion redistribution effect. Due to these properties, Li-Cu cells with the n-NbO<sub>2</sub>-coated separator show the most outstanding cycle stability with high Coulombic efficiency (CE) over 200 cycles.

## 1. Introduction

With the global interest in clean energy and growing environmental concerns, the electrification of the transportation sector has been considered a favorable strategy to reduce greenhouse gas emissions and other hazardous pollutants [1,2]. Nowadays, electric vehicles (EVs) are powered by Li-ion batteries (LIBs) owing to their distinctive properties such as good cyclability, long life span and few maintenance requirements [3]. However, the specific energy density of current commercial LIBs is in the range of 100–150 Wh kg<sup>-1</sup>, which is insufficient to provide EVs with a decent driving range compared with vehicles based on internal combustion engine [3–8]. Hence, it is necessary to develop high-energy-density batteries.

Li metal is a promising next-generation anode material for rechargeable batteries due to its high specific capacity (3,860 mAh g<sup>-1</sup>) and low redox potential (−3.04 V vs standard hydrogen electrode) [3,6,9–15]. Despite its superior characteristics, Li metal anode undergoes a considerable volume change during recurring Li plating/stripping processes owing to its host-less nature [7]. The resulting physical variation causes the breakdown/restoration of the solid

electrolyte interphase (SEI) layer on the anode surface [7,9,12,16]. This phenomenon accelerates electrolyte depletion and side reactions occurring between the Li metal anode and the electrolyte [7]. Moreover, Li-ion flux is significantly localized through the cracks in the SEI layer during Li plating, resulting in the formation of sharp dendritic Li [7,16,17]. The physical characteristics of the formed dendritic Li can lead to the penetration of the polyolefin separator, which substantially increases the risk of short-circuits [11,17,18]. Owing to these severe challenges, the pragmatic use of Li metal anode has been impeded in the industrial battery market for ~ 40 years [7,17]. To address the inherent issues of Li metal anodes, several approaches have been adopted, such as interface modification for stabilizing the Li metal electrode, construction of hosts that accommodate and regulate the expansion of Li, and introduction of three-dimensional current collectors [10–13,16,19]. Unfortunately, with the aforementioned strategies, it is technically difficult to achieve both reproducibility and scalability, hindering the industrial-scale deployment of LMBs [3,11]. Of all the existing strategies, the modification of commercial separators using functional materials has been considered an effective approach to overcome the intrinsic problems associated with the use of Li metal anode, owing to its

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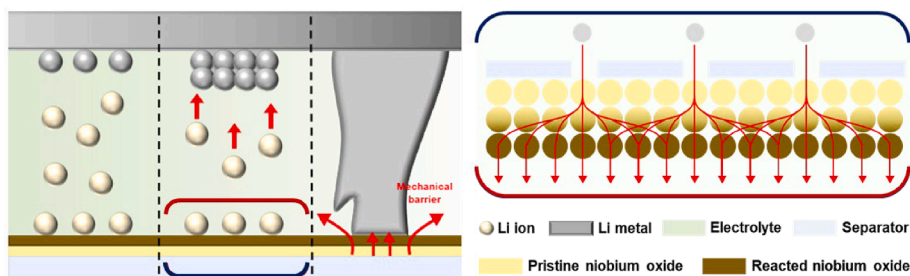


Fig. 1. Schematic illustration. The dendrite-inhibition behavior of niobium oxide-coated separator in LMB.

methodological advantages [3,10,11,13,18]. In this regard, several researchers have deposited various functional materials ( $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$ , graphene, etc.) onto separator [5,20–22]. Nevertheless, additional research is still necessary to achieve extended cycle life and mitigate parasitic reactions existing in LMBs [13,19].

In this article, we present a method for altering separators by coating a niobium oxide with superior electrical conductivity onto the PP separator. Niobium pentoxide ( $\text{Nb}_2\text{O}_5$ ) can react with Li metal, enabling intimate contact with the Li metal anode. However, insulation property of  $\text{Nb}_2\text{O}_5$  causes an increase in the internal resistance of the cell. As a strategy toward developing a niobium oxide layer with a high electrical conductivity,  $\text{NbO}_2$ , which has metallic conductivity, was introduced over the PP separator. Along with the advantage of electrical conductivity, a zero-strain property of  $\text{NbO}_2$  also reduces the delamination risk, which allows coating layer to adhere stably on the separator [23]. In addition, nitridation was conducted on the  $\text{NbO}_2$  to further improve the electrical conductivity. The highly enhanced electrical conductivity of n- $\text{NbO}_2$  promotes the Li plating/stripping process, expanding the intimate contact areas between the n- $\text{NbO}_2$  coating layer and the Li metal anode. Therefore, the n- $\text{NbO}_2$ -coated separator reinforces Li-ion redistribution

effects, leading to the best cycle stability over 200 cycles in Li-Cu cell.

## 2. Materials and methods

### 2.1. Nitridation process

The nitridation process was achieved using a horizontal tube furnace. For the nitridation process, approximately 1 g of the  $\text{NbO}_2$  powder was placed on an alumina boat. To reduce the detrimental effects of additional oxidation, a ceramic tube was fully deoxygenated by  $\text{N}_2$  purge for 1 h. The nitridation was performed in a high-purity nitrogen and ammonia atmosphere at 650 °C for 3 h. The flow rate of the nitrogen and ammonia mixture was maintained at 1 L  $\text{min}^{-1}$ .

### 2.2. Preparation of metal oxide-coated separator

The microporous membrane for niobium oxide coating was a commercially available PP separator (Celgard 3501, CELGARD, Charlotte, North Carolina, USA). The niobium oxide coating was performed by the blade-casting method. The 90 % niobium oxide powder, 10 %

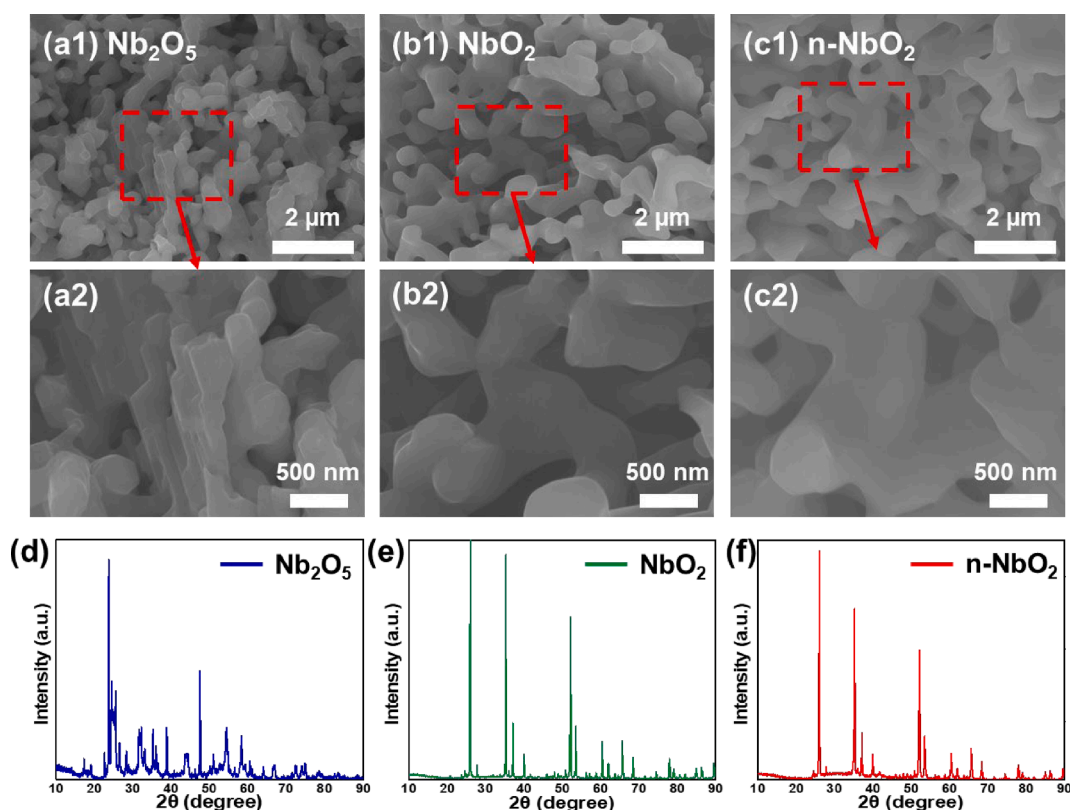


Fig. 2. Characterization. (a1-c1) Low-magnification SEM images of the  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and n- $\text{NbO}_2$  powder; (a2-c2) high-magnification SEM images of the boxed zones in a1-c1. (d-f) XRD patterns of the  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and n- $\text{NbO}_2$  powder.

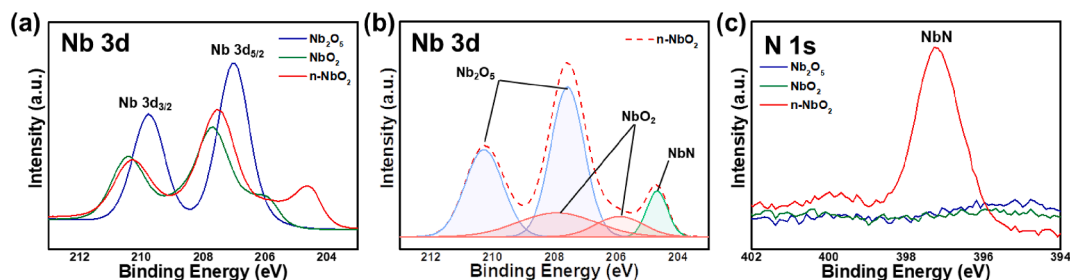


Fig. 3. XPS analysis on the surfaces of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$ . (a) Nb 3d XPS spectra; (b) fitted spectra of  $n\text{-NbO}_2$  in a, and (c) N 1 s XPS spectra.

PAA and additional deionized water were mixed using a planetary mixer to prepare the coating slurry. The slurry was coated onto the PP separator with its thickness adjusted to 10  $\mu\text{m}$ . The coated separators were dried overnight in a vacuum oven maintained at 50  $^\circ\text{C}$ .

### 2.3. Characterization

The electrical conductivity and resistance of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$  were estimated using a Powder Resistivity Analyzer (HPRm-01, HANTECH, Korea). Field emission scanning electron microscopy (FE-SEM, SU8220, Hitachi, Japan) was conducted to investigate the morphologies of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$  and  $n\text{-NbO}_2$ . To confirm the crystalline properties of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$ , X-ray diffraction (XRD, D8 Advance, Bruker, USA) was performed. UV–VIS impedance spectra were obtained using a UV–VIS spectrophotometer (V-770, JASCO, Japan). The compositional differences between  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$  were identified by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, ULVAC-PHI Inc, USA).

### 2.4. Measurement of electrochemical performance

To evaluate the electrochemical measurements, the 2032R-type coin cells were fabricated in a dry room with a dewpoint below  $-50\text{ }^\circ\text{C}$ . To investigate the electrochemical performances of each separator, Li–Cu cells were assembled with 1.0 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in a mixture of ethylene carbonate and diethyl carbonate (EC:DEC = 1:1 vol%) as the electrolyte and a 1.0 T Li metal foil as the counter electrode. The areal capacity for Li deposition and the cutoff voltage for Li stripping were set to 1.0  $\text{mAh cm}^{-2}$  and 1.0 V, respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed at frequencies ranging from 250 kHz to 10 MHz using a potentiostat (VSP, Biologic, Seyssinet-Pariset). The EIS parameters of the cells were calculated by the equivalent circuit in Fig. 5 (e). Li/Li symmetrical cells were assembled with two identical 1.0 T Li metal electrodes.

## 3. Result and discussion

Fig. 1 shows the dendrite-inhibition behavior of the niobium oxide

coated separator in LMB application. Niobium oxide is one of the few available metal oxides that can be applied to separator coating against Li metal anode [24,25]. Niobium oxide can interact with Li metal, enabling the coating layer to intimate contact with the Li metal anode and thereby redistribute the Li ions. Since the niobium oxide coated separator provides a uniform Li ion flux, the propagation of dendritic Li can be effectively suppressed. Furthermore, the niobium oxide coating layer can mechanically protect the separator from the uncontrolled dendritic Li. Despite these advantages, almost all metal oxides suffer from low electrical conductivity, leading to an increase in the electrode resistance. In particular, the insulation property of  $\text{Nb}_2\text{O}_5$  can be confirmed from its wide band gap energy of 3.1 eV (SI Section 1). To overcome the limited electrical conductivity,  $\text{NbO}_2$ , which is classified as a n-type semiconductor, was introduced [26]. Additionally, the electrical conductivity of  $\text{NbO}_2$  was further improved through nitridation process. The measured resistance and conductivity of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$  are shown in SI Section 2. The improved electrical properties of  $n\text{-NbO}_2$  facilitate the Li plating/stripping process, which enlarges contact areas between the coating layer and the Li metal anode. Therefore, the  $n\text{-NbO}_2$ -coated separator can strengthen the Li ion redistribution effects compared with  $\text{Nb}_2\text{O}_5$ -coated separator.

Fig. 2(a1)–(c1) show the morphologies of all the prepared niobium oxides obtained by SEM. To investigate the differences in the crystal structure, each SEM image was magnified (Fig. 2(a2)–(c2)). Based on the morphology of  $\text{NbO}_2$ ,  $\text{Nb}_2\text{O}_5$  crystallized into euhedral particles that were some micrometers with striated edges which is corresponded with monoclinic phase  $\text{Nb}_2\text{O}_5$  ( $\text{H-Nb}_2\text{O}_5$ ) [27]. Meanwhile, the morphology of  $n\text{-NbO}_2$  was largely the same as that of  $\text{NbO}_2$ , without any crystallization. Additionally, there was no agglomeration of the  $n\text{-NbO}_2$  particles since the nitridation process was performed under a mild condition. To ascertain this result, the XRD patterns of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$  were obtained, as shown in Fig. 2(d)–(f). The XRD results of  $\text{Nb}_2\text{O}_5$  and  $\text{NbO}_2$  correspond to the two references of  $\text{H-Nb}_2\text{O}_5$  and  $\text{NbO}_2$ , respectively (ICDD, #00–037-1468 and #00–043-1043). Likewise, Fig. 2(f) shows that the XRD patterns of  $n\text{-NbO}_2$  match with the  $\text{NbO}_2$  phase. This result also supports the fact that there was no crystalline change in  $n\text{-NbO}_2$  during the nitridation process.

To verify the successful implementation of the nitridation process on

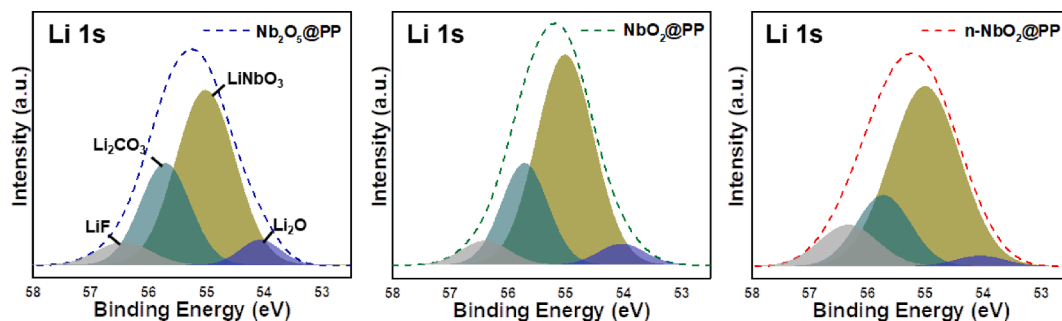


Fig. 4. Verification of electrochemical reaction between niobium oxide and Li metal. XPS spectra of Li 1 s on the surfaces of  $\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ , and  $n\text{-NbO}_2$  coating layers facing with Li metal anode after 1 cycle.

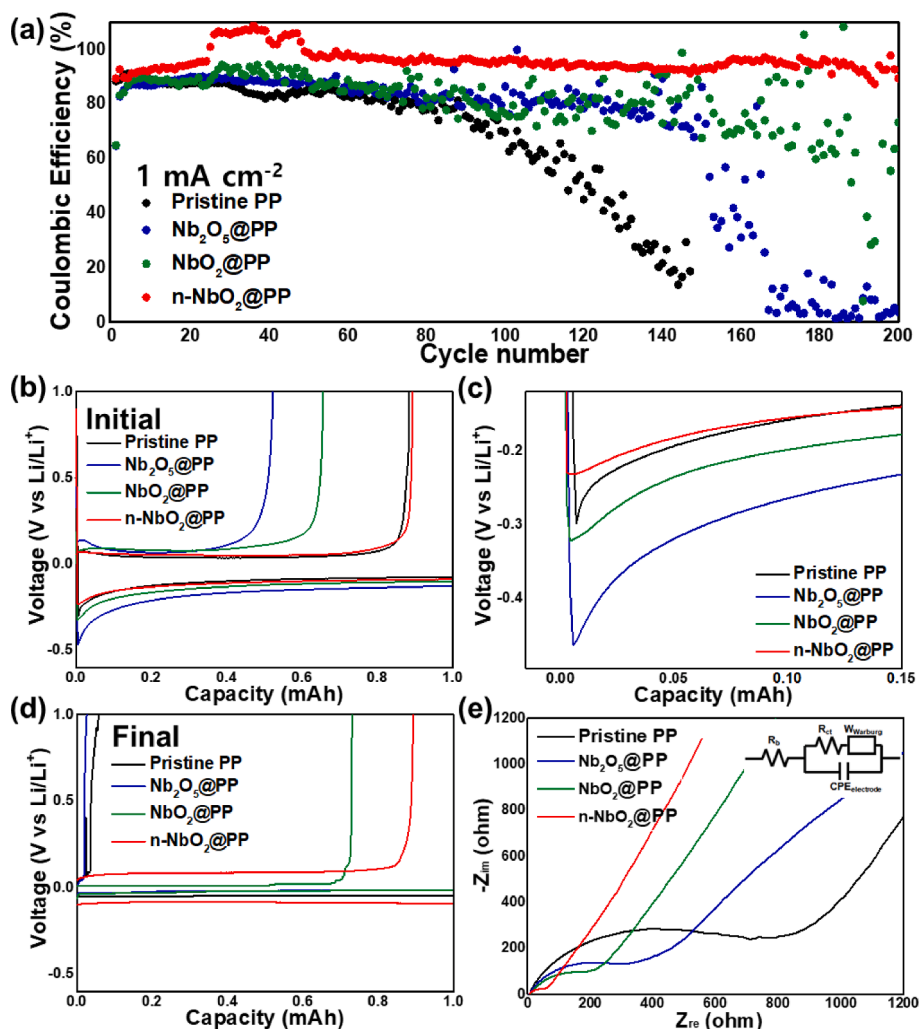


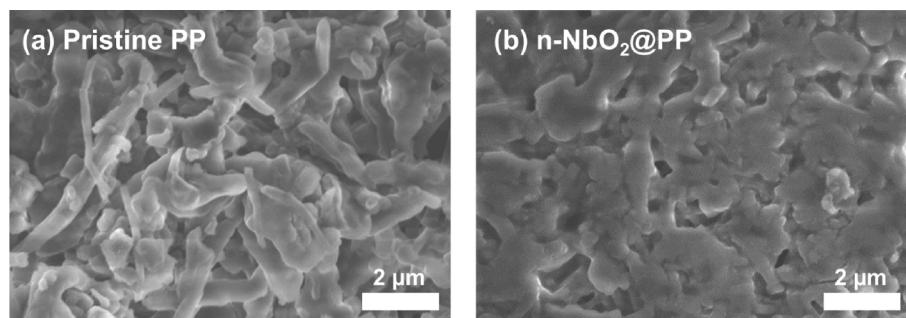
Fig. 5. Electrochemical performances of Li-Cu cells with the pristine PP separator,  $\text{Nb}_2\text{O}_5$ -,  $\text{NbO}_2$ -, and  $n\text{-NbO}_2$ -coated separators. (a) Cycling performances of each cell at a current density of  $1 \text{ mA cm}^{-2}$ . Voltage profiles of each cell in (b and c) the 1st cycle and (d) 200 cycles. (e) EIS spectra of each cell after cycling.

$\text{NbO}_2$ , the chemical compositions of the niobium oxides were investigated by XPS analysis, as shown in Fig. 3. In the Nb 3d spectra, two distinct components can be identified for all samples. (Fig. 3(a)) The peaks at  $\sim 207$  and  $\sim 210$  eV correspond to the Nb  $3d_{5/2}$  and Nb  $3d_{3/2}$ , respectively [28]. These peaks are related to typical  $\text{Nb}_2\text{O}_5$  phases. It should be noted that an XPS analysis provides more sensitive results of the surface state than an XRD analysis. Since surface oxidation occurs after exposure to air, the  $\text{Nb}_2\text{O}_5$  phase exists in  $\text{NbO}_2$  and  $n\text{-NbO}_2$  powder. From the fit of the  $n\text{-NbO}_2$  powder, two other components can be found, associated with  $\text{NbO}_2$  and niobium nitride (NbN) (Fig. 3(b)) [29,30]. The ratio of the doublets ( $\text{Nb}_2\text{O}_5/\text{NbO}_2$ ) of the  $n\text{-NbO}_2$  powder was largely similar to that of  $\text{NbO}_2$ , which is shown in SI Section 3. This indicates that only pure nitrogen was doped into  $n\text{-NbO}_2$  without additional oxidation during the nitridation process. Additionally, the high-resolution N 1s spectra is shown in Fig. 3(c), in which the only peak of  $n\text{-NbO}_2$  at 397 eV is from the NbN phase. The existence of superconductive NbN [31] in  $n\text{-NbO}_2$  is further evidence of the successful nitridation.

The above-mentioned notion about Li ion redistribution effect is on the basis that electrochemical reactions are performed between the niobium oxide and metallic Li. To verify this, the chemical composition of niobium oxide coating layer disassembled from the Li-Cu half cells was analyzed after 1 cycle (Fig. 4). From the XPS spectra of Li 1s, SEI peaks and  $\text{LiNbO}_3$  peak can be detected on the surface of all niobium oxide coating layers [32].  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$  and  $\text{LiF}$  are major species of SEI

originating from the decomposition of the liquid electrolyte. Especially,  $\text{LiNbO}_3$  is one typical evidence of the interaction between niobium oxide and metallic Li. These results indicate that niobium oxides electrochemically interact with metallic Li, resulting in intimate contact between coating layer and Li metal anode. Therefore, an abundant 3D ion conduction channels are formed within each coating layer, contributing to effective Li ion redistribution effects. In other words, it can be inferred that niobium oxide-coated separator is helpful for suppressing the dendritic Li by maintaining the uniform Li ion distribution.

To investigate the electrochemical performance of the niobium oxide-coated separator on the LMB performance, the Li-Cu half cells were evaluated at  $1.0 \text{ mA cm}^{-2}$ . Fig. 5(a) shows the cycling data of the Li-Cu half cells. As the severe growth of dendritic Li causes “dead Li”, the cell with the pristine PP separator decays rapidly, and the CEs gradually decreases after 80 cycles. In contrast, the stable CEs of the cells with the  $\text{Nb}_2\text{O}_5$ - and  $\text{NbO}_2$ -coated separators are maintained until 150 cycles. This can be attributed to the fact that the niobium oxide coating layer not only physically suppresses dendritic Li overgrowth but also serves as a Li absorbent to redistribute the localized Li ion flux [26,33]. Unlike the Li-Cu cells with the  $\text{Nb}_2\text{O}_5$ - and  $\text{NbO}_2$ -coated separators, the cell with the  $n\text{-NbO}_2$ -coated separator exhibits the most stable cycle performance with high CE (90%) during 200 cycles. To better understand the mechanism whereby the  $n\text{-NbO}_2$ -coated separator enhances the cell efficiency, the initial galvanostatic charge/discharge curves of each Li-Cu cell are compared in Fig. 5(b) and (c). The cells with the  $\text{Nb}_2\text{O}_5$ - and



**Fig. 6. Post-mortem examinations of cells after cycling.** SEM images of the cycled Li metal anodes with (a) the pristine PP separator and (b) n-NbO<sub>2</sub>-coated separator.

NbO<sub>2</sub>-coated separators exhibit a higher overpotential compared to the cell with the pristine PP separator, due to the low electrical conductivity observed in metal oxides. In a galvanic cell, the overpotential is directly associated with the cell efficiency. The high overpotential of the cells with the Nb<sub>2</sub>O<sub>5</sub>- and NbO<sub>2</sub>-coated separators lead to a low cell efficiency, ultimately causing cell failure. Meanwhile, the cell with the n-NbO<sub>2</sub>-coated separator exhibits the lowest overpotential owing to enhanced electrical conductivity of n-NbO<sub>2</sub>. The improved electrical conductivity of n-NbO<sub>2</sub> promotes the Li plating/stripping processes and reduces the interfacial resistance, thus eventually reinforces the Li redistribution effect. For these reasons, the cycle retention of the cell with the n-NbO<sub>2</sub>-coated separator exceeds those of the other cells at 200 cycles (Fig. 5(d)).

Fig. 5(e) shows the electrochemical impedance spectra (EIS) of each Li-Cu cell at 150 cycles. The inset illustration represents an equivalent circuit used to fit the EIS data. In the equivalent circuit,  $R_b$  is the bulk resistance of the cell,  $R_{ct}$  is the interfacial resistance related to charge transfer, CPE is double layer capacitance affected by surface roughness of electrode and  $W$  is Warburg impedance associated with the Li ion diffusion [34]. Each value of EIS data is fitted and summarized in SI Section 4. Since the  $R_{ct}$  is much larger than  $R_b$ , it dominates the overall internal impedance of cells. Based on the abovementioned advantages, the cell with the n-NbO<sub>2</sub>-coated separator exhibits the lowest  $R_{ct}$  (76.8  $\Omega$ ) compared to other cells. To further enhance the reliability of results, symmetrical cell test was conducted (SI Section 5). The overpotential of symmetrical cell with the pristine PP separator is initially maintained at  $\approx 0.13$  V and gradually increases to  $\approx 0.25$  V, which could be explained by the accumulation and destruction of SEI owing to formation of dendritic Li. In contrast, the symmetrical cell with the n-NbO<sub>2</sub>-coated separator maintains a stable overpotential. These results are considered that the n-NbO<sub>2</sub>-coated separator effectively inhibits dendritic Li growth and contributes to the outstanding electrochemical reversibility.

To confirm the stability of the Li metal anode, the surface structural evolution of the Li metal anodes was investigated after 200 cycles. Fig. 6 (a) and (b) show the SEM images of the cycled Li metal anodes with the pristine PP separator and n-NbO<sub>2</sub>-coated separator, respectively. Extensive rod-like Li clusters are observed in the Li metal anode with the pristine PP separator. These morphologies correspond to the accumulation of dendritic Li, which eventually penetrate the separator and cause safety issues. In contrast, the Li metal anode with the n-NbO<sub>2</sub>-coated separator exhibits a smooth surface without any visible dendritic Li. It is attributed to its reversible capability originating from the Li redistribution effect. These results are also observed in the low magnification SEM images which is shown in SI Section 6. From these results, it can be inferred that the n-NbO<sub>2</sub> coating layer effectively suppresses the growth of dendritic Li and protect the separator. Therefore, the n-NbO<sub>2</sub> coating layer plays a significant role in inhibiting the formation of dendritic Li and stabilizing the cycle performance of LMBs.

#### 4. Conclusion

In this study, we introduced n-NbO<sub>2</sub> as a coating layer on a separator to suppress the growth of dendritic Li in LMB. Niobium oxide coating layer reacts with Li metal anode and constructs the intimate contact, leading to the Li ion redistribution effect. Furthermore, due to the superior electrical conductivity, the n-NbO<sub>2</sub>-coated separator can reinforce the Li ion redistribution effect within the separator, compared to other separators. Based on these property, n-NbO<sub>2</sub>-coated separator most effectively regulates the Li-ion flux over the electrode, thereby suppressing the propagation of dendritic Li. Therefore, the Li-Cu cell with the n-NbO<sub>2</sub>-coated separator achieved the most outstanding electrochemical performance. We believe that our strategy would address the problems related to the unstable mechanisms of Li metal anode and represents a diverse approach for separator modification in LMBs.

#### CRediT authorship contribution statement

**Junghwan Kim:** Conceptualization, Visualization, Writing – original draft. **Kihwan Kwon:** Investigation, Resources, Writing – original draft. **Kwangchul Roh:** Visualization. **Jiseok Kwon:** Validation. **Tae-seup Song:** Investigation. **Patrick Joohyun Kim:** Supervision, Writing – review & editing. **Junghyun Choi:** Supervision, Project administration, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgement

This work was supported by the Technology Innovation Program (20010960) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2021R1F1A1059892).

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