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Expeditious Full Discharging Method without Voltage Rebound Issue for Safe Battery Recycling

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ABSTRACT

To achieve recycling without safety hazards by explosion of spent batteries, an efficient full discharging procedure is required to stabilize the batteries before recycling. However, typical salt solution discharging technique has environmental pollution, inefficiency, and safety issues due to wastewater emission, slow discharging rate, and severe voltage rebound. Electrical discharging techniques can be applied to overcome these problems, but the typical constant-current and constant-current constant-voltage modes have a trade-off relationship between discharge time and voltage rebound. In this study, we propose reverse voltage mode as an expeditious and safe electrical discharging protocol that effectively addresses the trade-off between discharging time and voltage rebound. The proposed reverse voltage mode for full discharging method was proven to be effective regardless of the electrode crystal structure or the battery form factor. This result is expected to present new methodology for pre-stabilization of spent batteries for more eco-friendly and stable recycling.

Keywords : Battery recycling, Full discharge, Reverse voltage mode, Electrical discharging technique, Voltage rebound

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1. Introduction

As electrical vehicles market continues to grow, it is expected that the magnitude of spent batteries will reach 3,339 GWh by 2040 (SNE Research). Treating spent batteries by landfill or incineration poses significant obstacles such as safety hazards (e.g., explosion, fire) and generation of toxic gases [1,2]. Moreover, owing to the finite nature of resources, concerns arise regarding potential depletion (e.g., Co depletion projected by IW-Consulting Group by 2032) and increase of Resource prices (expected that price of Li_2CO_3 continuously increased after 2028, SNE Research).

In this circumstance, comparing the number of explosion incidents with EV and spent battery, it is reported 18.4 and 57 incidents per each year (EPA, An Analysis of Lithium-ion Battery Fires in Waste Management and Recycling). However, the safety of spent batteries is often less emphasized compared to the safety of electric vehicle (EV) batteries (Fig. 1A) [3–5]. As safety hazards could be generated with only small amount of external force, safety of spent batteries is important. In addition, safety issues with spent batteries can more easily arise due to degradation of electrodes and separators [6]. Therefore, strategy for safe transport, storage, and recycling is necessary to be importantly considered.

The recycling process of spent batteries is divided into pre-treatment process [7,8] that producing black powder [9], and subsequent process that aims to recover the valuable metals from black powder (hydrometallurgy) or resynthesis the cathode active materials (direct recycling) [10,11]. However, it is noteworthy that the residual energy present in spent batteries may lead to risks such as explosion or fire during pretreatment process [12]. Consequently, to ensure the safe recycling, discharging protocol that could minimize the residual energy must be developed.

The safety of the recycling process relies on methods such as salt solution discharge, battery deactivation via external short circuits, inert-state crushing,

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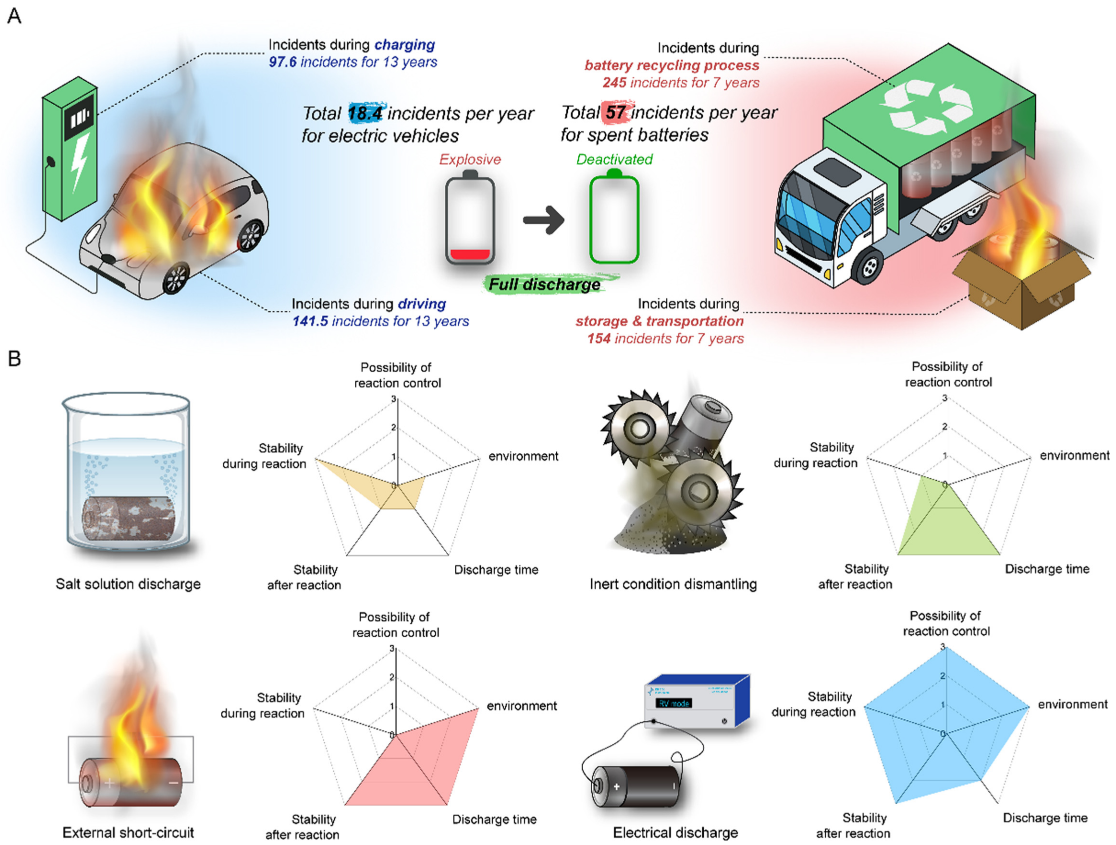

Fig. 1. Importance of electrical discharging method for safe spent battery recycling. (A) Safety hazards of electric vehicles batteries and spent batteries; (B) Four discharging method and characteristic of each method.

and electrical discharging [13–16]. Among these methods, salt solution discharge is widely adopted in the industry, wherein salts like NaCl are dissolved in a solution and used to deplete the residual energy within batteries through water electrolysis reactions [17]. However, it faces drawback about non-guarantee of safety; during the rest process after completing electrolysis reactions, the voltage rebound is observed due to the overpotential, indicating an incomplete reduction of safety hazards for spent batteries [18]. Furthermore, the issues of corrosion and generation of wastewater must be considered in conjunction with the degree of voltage rebound [19]. Alternatively, methods inducing short circuits through electrical conductors result in generating a significant amount of joule heat, leading to fire and explosion risks, as the entire electrochemical reaction occurs simultaneously [20]. Inert-state crushing poses challenges in terms of facility and cost requirements to maintain an inert state, with the significant drawback of toxic gas generation during reactions [21].

To solve these problems, methods utilizing electrical discharging, which employ current to eliminate residual energy in spent batteries, can be introduced. However, with conventional constant-current (CC) and constant-current constant-voltage (CC-CV) mode, the trade-off relationship between discharging time and voltage rebound emerges as a critical obstacle for commercialization. Consequently, innovative breakthroughs are necessary to be suggested that could minimize both discharging time and voltage rebound. Thus, in this study, reverse voltage (RV) mode that maintains voltage of cell under 0 V is introduced. Utilizing this mode, with short time discharging, voltage rebound is extremely low even when the battery is neglected for 48 hours after the discharging; trade-off between discharging time and voltage rebound is successfully addressed. The application of this expeditious and safe method in spent battery recycling enables reducing the safety hazards of spent batteries. Furthermore, with the insights derived from this electrical discharging protocol, we can find broad applicability in achieving full discharge of LIBs.

2. Experimental

2.1 Materials

The following materials were used as purchased without further purification and stored under Ar: PVdF (average Mw ≈ 534 000 by GPC, SOLVAY), lithium metal foil (0.2 mm thick, Honjo Metal Co.), and 1 M $LiPF_6$ in EC/DMC (1:1 v/v, Donghwa electrolyte). NCM811 (LG Chem), NCM622 (L&F), LFP, and Super P (>99%, Alfa Aesar) were dried at 120°C in a vacuum oven for 3 days. Separator was dried at 40°C in a vacuum oven for 3 days.

2.2 Cell fabrication

Active material, Super P (conductive material), and PVdF (binding material) in NMP were mixed in the respective weight ratio 90:5:5 (for NCM) and 8:1:1 (for LFP) using a Thinky mixer (AR-100) at 2000 rpm for 20 min and then coated onto Al current collectors. After drying at 120°C in a vacuum oven for 12 h, the electrode was punched into circular discs (φ = 12 mm). The mass loading of NCM was 7.5–8.5 mg cm^{-2} and 2.5–3.5 mg cm^{-2} for LFP. CR2032 coin-type cells were assembled using a separator (φ = 19 mm), a NCM electrode as the working electrode, and a lithium metal foil as the counter electrode (φ = 16 mm). 1 M $LiPF_6$ in EC/DMC (1:1 v/v) 200 μm electrolyte was used for each coin cell. For the fabrication of pouch cells, electrodes with area 5 cm^2 and 12 cm^2 were used.

2.3 Electrochemical test

All electrochemical methods were performed at 25°C using a potentiostat (WBCS3000, WBCS3000Ls, WonATech) for galvanostatic methods. The cells were treated after standing at the open-circuit voltage for 12 h. Galvanostatic intermittent titration technique (GITT) was conducted with the schedule of 10 minutes charge or discharge with 18 mA g^{-1} and 50 minutes rest. Galvanostatic charge discharge result was obtained after 1 cycle of formation with charge cut-off potential 4.3 V, and discharge cut-off potential 2.7 V. Reverse voltage mode was conducted for 1 h 30 m with 5 C rate. Cut off voltage was set to –1 V, but the potential during RV mode did not reach –1 V and exhibited $-1\ V < x < 0\ V$.

2.4 Characterization

Before the being transferred for XRD and SEM, electrodes recovered with disassembling of cells were sealed in an airtight container inside the glovebox. The XRD patterns were obtained by an X-ray diffractometer (Rigaku, SmartLab) with a 9 kW Cu target at a scan rate of 1° min^{-1} within 2θ range of 10–80°. SEM measurements were performed using a JSM-7800F Prime (JEOL).

3. Results and Discussion

3.1 Novel discharging method for short discharging time and low voltage rebound

Analyses for comparison were conducted to identify the optimal discharge method for ensuring the safety of spent battery recycling process through electrical discharge. The first step was to understand the tendency of overpotential during the discharge process and its correlation with discharging rate. It was hypothesized that the overpotential at the end of the discharge process would directly affect to voltage rebound [22]. Therefore, GITT analysis was conducted at various discharging rates to establish strategies for minimizing voltage rebound (Fig. 2A, Supplementary Fig. 1). In all experiments, the discharging rates were set based on the capacity within the reversible range of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), from 2.7 to 4.3 V. Fig. 2A illustrates that even under same reactions, different overpotential is observed depending on the discharging rate. Comparing GITT results at 0.1 C and 1 C, a notable increase in overall overpotential is observed when driven at 1 C. Fig. 2B depicts overpotential concerning operating voltages at 0.1, 0.5, 1, and 3 C. Overpotential generally exhibit converging to each constant value for each C-rate condition. Consequently, voltage rebound depends on the discharging rate, which indicate that achieving a low voltage rebound with a short discharge time is challenging. However, after the 600 hours (0.1 C-rate, 60 hours for 1 C-rate) in GITT experiment as shown in blue region Fig. 2A, it was observed that the tendency of overpotential and voltage rebound drastically changed under the 0 V

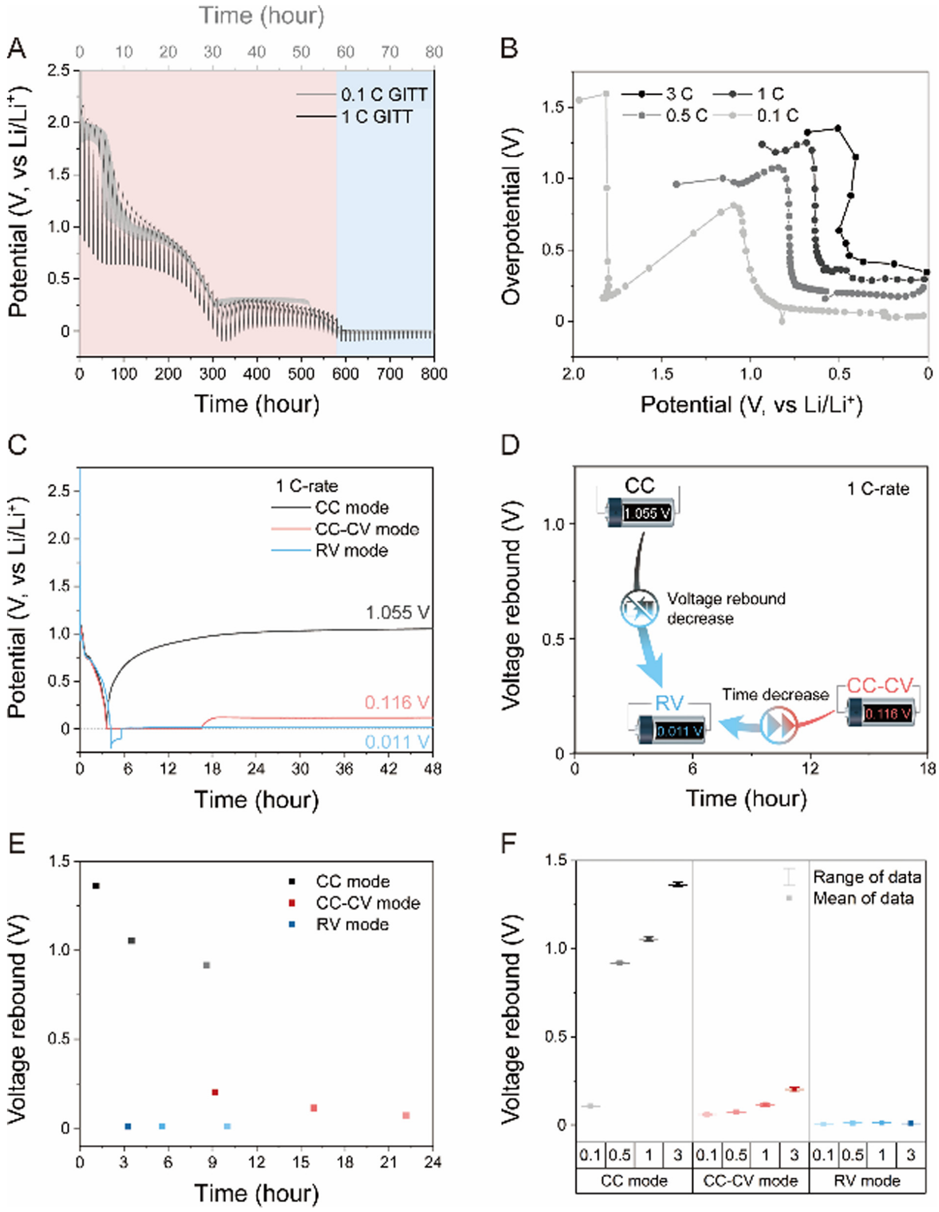

Fig. 2. Reverse voltage mode for short discharging time and low voltage rebound. (A) GITT result with 0.1 C, 1 C rate conditions; (B) Relationship between discharging rate and overpotential; (C) Voltage rebound comparison with three types of discharging mode; (D) Schematic illustration about advantage of reverse voltage mode; (E) Voltage rebound with various discharging mode at various rate (0.5 C, 1 C, 3 C); (F) Average of voltage rebound test results with various discharging mode and discharging rate.

(vs Li/Li^+). Region under the 0 V (vs Li/Li^+), while higher C-rate result in larger overpotential, it is observed that during rest periods, the potential converges to 0 V independent of the C-rate. We identified such phenomenon and understood that achieving a full discharge method that minimizes rebound with short discharging is over-discharging of cell to the region of reverse voltage.

To assess the effectiveness of the RV mode as a full discharge method, we conducted experiment and compared the results of discharging time and voltage rebound of three different modes (Fig. 2C and D, Fig. S3–S7). Under the 1 C condition, the time required for discharge in each mode was 3 hours and 45 minutes for CC, 16 hours and 32 minutes for CC-CV, and 5 hours and 44 minutes for the RV mode, with corresponding voltage rebounds of 1.055 V, 0.116 V, and 0.011 V. Additionally, CC-CV mode, while expected to yield lower overpotential due to decreased current during the CV process, is confirmed to require longer discharge time as CV mode gradually decreases the current. The results of CC mode and CC-CV mode showed the difficulty of achieving both short discharge times and low voltage rebounds simultaneously, highlighting the importance of the RV mode in achieving this dual purpose. In other words, RV mode is the strategy that could offset the trade-off between discharging time and voltage rebound. Degree of voltage rebound was examined initially under various conditions (Supplementary Fig. 2). Discharging the cell with high current value (5 C-rate) shows significant meaning of RV mode; break the trade-off relationship unlike conventional CC mode. Also, remarkable effect was shown with 1 hour 30 minutes discharging condition. As shown in Fig. 2E, both CC and CC-CV modes exhibited increasing voltage rebound with higher discharge rates, while the RV mode maintained a small voltage rebound even when conducting high-rate discharge. Fig. 2F, representing the deviation of results after three times experiments at various rates, shows minimal variation with three modes, and further confirms the reliability of those three modes. More detailed information about statistic is in supporting information.

3.2 Possibility of commercialization of reverse voltage mode

To verify the effect of RV mode in actual recycling processes, it was necessary to confirm the results with different structures and compositions of cathode materials, and whether it could be applied without problems on a larger scale. Therefore, NCM622 (with lower nickel content) and LFP (olivine crystal structure) was applied to confirm the feasibility of this strategy. With NCM622 (Fig. 3A), RV mode exhibits lowest voltage rebound compared to CC mode and CC-CV mode, similar to NCM811. This phenomenon appears from the similarity of structural and reaction mechanism despite differences in transition metal contents. In the case of LFP (Fig.

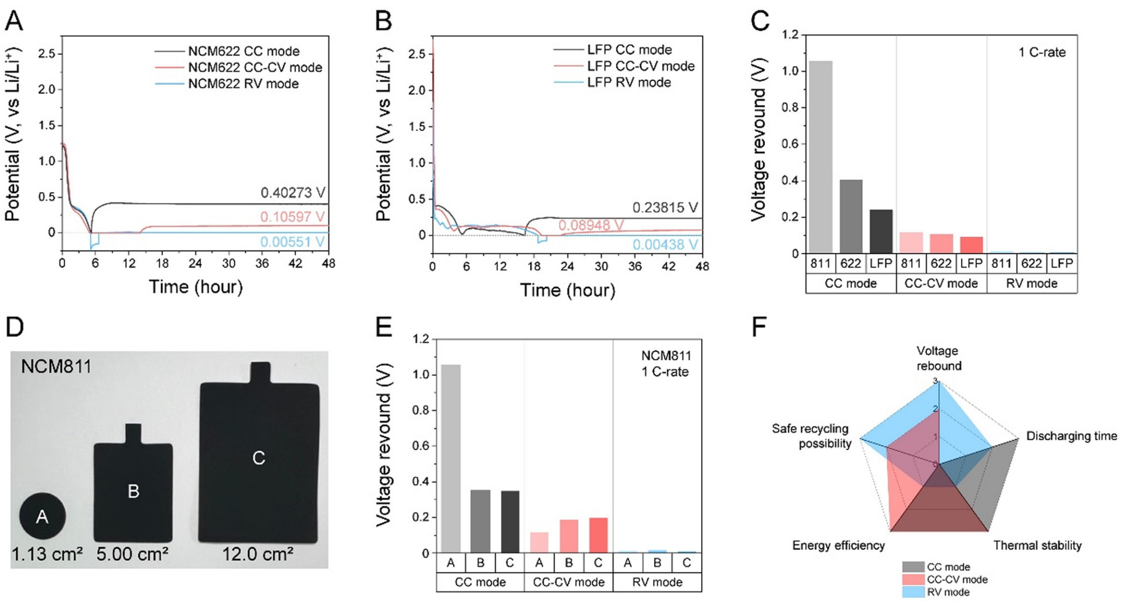

Fig. 3. Reverse voltage mode enabling the commercialization. Results of (A) Utilizing LFP; (B) Utilizing NCM622; (C) comparison of results using various composition and structure of cathode; (D) Enlarged electrode adopted for test; (E) Voltage rebound result with various size of electrode; (F) Characteristic comparison of three electrical discharging modes.

3B), with an olivine structure and distinct electrochemical reactions, voltage rebound was minimized with short discharging time by applying the RV mode. The results obtained from three type of cathode material are plotted in Fig. 3C, which signify that RV mode can be applicated regardless of the type of cathode. To demonstrate the commercial application of RV mode, larger sized electrodes using pouch-type cell were adopted (Fig. 3D). Regardless of the size of electrodes, the voltage rebound with the RV mode was observed significantly smaller compared to the other two modes, similar with that observed with an area of 1.13 cm^2 (Fig. 3E, Fig. S8). These results imply the applicability of the RV mode even in large-scale cells for commercial recycling processes of spent batteries. A spider map is presented at Fig. 3F to quantitatively compare the characteristics of each mode for electrical discharging in this study. When comparing discharge time, CC mode has the shortest discharge time, while the CC-CV mode requires the longest discharging time. Similarly, assessing one of the crucial factors, the voltage rebound after discharging was observed the highest value with CC mode, while the least with the RV mode. Since voltage rebound is directly related to safety concerns, the introduction of the RV is essential for ensuring safety. When comparing the energy efficiency and thermal stability, it is shown that RV mode exhibits slightly higher values, whereas CC mode shows lower values. These comparative findings elucidate how the effect of RV mode aids in overcoming the trade-off relationship between voltage rebound and discharging time. The detailed explanation is on Supporting Information.

3.3 Various application area of novel reverse voltage mode

As illustrated in Fig. 4, the RV mode may be considered for the expansion in various directions. First, it has been verified that it could be utilized independent of cathode type. Additionally, by conducting studies at the various scales, as exemplified by coin-type cells and pouch-type cells, it has been shown that RV mode enables the full discharge of practical larger systems. Finally, this strategy aimed at mitigating the trade-off between discharging time and voltage rebound would contribute to laying the groundwork for exploring enhanced full discharging strategies tailored to diverse battery systems.

4. Conclusions

In this study, RV mode is introduced to ensure the safety during the recycling of spent batteries by minimizing overpotential. Unlike CC mode and CC-CV mode, RV mode noticeably mitigates the trade-off relationship between discharging time and voltage rebound. Moreover, this strategy can be utilized regardless of electrode crystal structures such as NCM or LFP, and even in scale-up considerations for practical applications, indicating effectiveness of RV mode. This research holds importance in guaranteeing the safety of battery recycling processes through variations in simple discharge methodologies. Despite various issues, it is believed that it could serve as a novel strategy for generating additional breakthroughs and results aimed at overcoming the current situation.

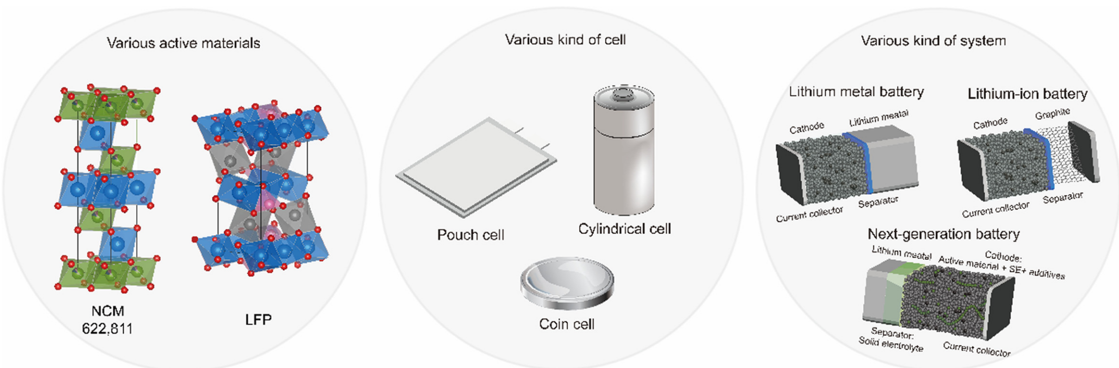

Fig. 4. Schematic illustration of RV mode with various applications.

Credit authorship contribution statement

Ji-Su Woo: conceptualized and designed the experiments, conducted experimental, conducted analysis, and wrote original draft. Hong-Geun Lee: conducted experimental, analysis, and wrote original draft. Keun-Ho Heo: conducted experimental. Geun-Ha Hwang: conducted analysis and wrote original draft. Yu-Chan Hwang: conducted analysis. Won-Jin Kwak: reviewed and edited the manuscript, and supervised the project.

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Supporting Information

Supporting Information is available at https://doi.org/10.33961/jecst.2024.00493

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