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One-Pot Spray Engineering to Design Na_{0.44}MnO₂ Cathode Electrodes for High-Rate and Cycle-Stable Na-Ion Batteries

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Abstract: To improve the practical performance of Na-ion batteries, electrode structure engineering provides a new route to improve the electrochemical efficiency of the cathode active material. In this study, we suggest a new route of one-pot spray engineering to design Na_{0.44}MnO₂ cathodes to realize high-rate and cycle-stable Na-ion battery performance. This technique adjusts the electrode structure from a dense to an open sponge-like morphology during layer-by-layer deposition of the materials. The sponge-like cathode results in improved ion insertion and transport kinetics, thus accelerating the rate capability with increased capacity and high-rate cycling capability (100.1 mAh/g and 90.2% cycling retention after 100 cycles at 5 C). These results highlight the potential for design engineering of cathode structures to achieve high-rate and cycle-stable performance for Na-ion batteries.

Keywords: sodium-ion battery; electrode structure; Na_{0.44}MnO₂; one-pot spraying construction; open-pores networking structure



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1. Introduction

As the use of renewable energy sources throughout the world increases to address net zero challenges, there is a rapidly increasing interest in battery applications that can store the intermittent electricity generated by these renewable sources. Lithium-ion batteries (LIBs) are the current widely used energy storage systems in applications ranging from portable electronic devices such as mobile phones, laptops, and cameras to large-scale devices such as electric vehicles and large-scale energy storage systems [1,2]. This accelerates the demand for lithium sources, which has caused its price to rise and threatened the possibility of its resource depletion [3]. The competition to develop easy-accessible, low-cost, and high-efficiency alternatives to the ubiquitous LIBs is progressing worldwide. Among these, sodium-ion batteries (SIBs) have received growing attention, which has resulted from the reserves of abundant sodium resources (2.83 wt%) compared to lithium (0.01 wt%) in the Earth's crust with reaction mechanisms and processing procedures similar to those of LIBs. In addition, sodium does not alloy with aluminum, and therefore aluminum foil can be used as the current collector for both the cathode and anode, which may replace the use of the more expensive and heavier copper as the current collector and is beneficial for realizing low-cost and large-scale applications with high gravimetric energy density. However, the larger ionic radius of sodium ions (1.02 Å) compared to lithium ions (0.76 Å) can negatively affect phase stability, transport properties, and interphase formation resulting in degradation of rate capability and cycling stability. The higher standard electrode potential of SIBs (−2.71 V vs. SHE in comparison with

–3.02 V vs. SHE for Li) also leads to reduced energy densities [4]. Therefore, the effort to improve the performance of SIBs based on an understanding of the electrochemical behavior of active materials and electrode structures should be explored [5].

In SIBs, cathodes have an important factor to determine their performance such as energy density and cycling life due to the relatively low specific capacity (100–200 mAh/g) compared to anodes (e.g., 250 mAh/g for hard carbon) [6–10]. There are challenges for successful cathode materials of SIBs to catch up with LIBs, including (1) ability to host a large number of Na ions; (2) high redox potential; (3) stable structural integrity during cycling; (4) large diffusion coefficient for Na ions and high electronic conductivity; (5) high chemical and thermal stabilities and compatibility with electrolytes; and (6) environmental friendliness and cost-effectiveness [11,12]. Among the pioneering developments of cathode materials of Na transition material oxide compounds ($\text{Na}_x\text{M}_y\text{O}_z$, M = Mn, Co, Ni, etc.), olivine phosphates, fluorophosphates, and Prussian blue analogs, [13–18], Na-Mn-O compounds have received an intensive attention for potential use in large-scale applications due to their high capacity, nontoxicity, and low cost [19]. The Na-Mn-O compounds can be classified into two kinds with layered and tunneled structures. For the layered structure (NaMnO_2 and $\text{Na}_{0.66}\text{MnO}_2$), it provides high specific capacity but limited cycling stability, whereas the tunneled structure exhibits good cycling stability but low specific capacity [20]. In addition, tremendous efforts have been tried for accelerating their performance through other research strategies, such as nanostructuring (e.g., nanorods [21], nanoplates [22]), surface modification (e.g., adding carbon or metal oxide layer [23]), and the introduction of multiple transition metals (e.g., Ni, Fe, and Ti [24–27]) to reduce electrical resistance, shorten Na ion diffusion paths, and improve interfacial comparability between electrode materials and electrolytes. However, although such extensive research of high-performance cathode materials delivers a hopeful message to raise the application possibilities of the SIBs, the mechanical and electrical failure relating to electrode-structural integrity is still an important issue that needs to be solved for the future battery industry.

High-rate cycling capability is an important factor for SIBs toward their applicability to practical products and a stepping stone for the development of the future battery industry [28,29]. During the charge and discharge process, unavoidable agglomeration and volume expansion of electrode materials and solid electrolyte interface (SEI) formation across the electrodes, trigger degradation mechanisms on the SIB performance. The uneven distribution of active materials restricts electron and ion diffusion due to carrier trapping centers formed from electrode-structural distortion, followed by electrode destruction at a larger scale with fractures, inducing extra SEI formation and detachment of the electrode from current collectors, resulting in inferior rate performance and poor cycling retention [30,31]. Modeling has provided important evidence of inherent problems at the electrode level that can threaten stability and battery performance due to partially applied overvoltage induced by the inhomogeneous occupation of Li ions and can suggest that these problems are also present in the electrodes of SIBs. The countermeasures used in LIBs include growing nano-arrayed architectures using Co_3O_4 on current collectors with void gaps for buffering structural variations [32] and fabricating hybrid structures possessing an oriented face-to-face arrangement of Si and graphene that features robust structural stability [33]. Unfortunately, these approaches rely on exquisite and complex manufacturing techniques that could limit industrial battery applications. As an example of breakthroughs, our group has reported novel strategies of electrode engineering to design unique structures of layer-by-layer electrodes with different fractions of conductive additive and directional porosity with low tortuosity using scalable spray printing and freeze-casting methods, beneficial to battery performance [34–41]. Although electrode design is a key factor in effectively facilitating ion mobility, the gap between the performance of active materials themselves and the performance relating to electrode structures remains unresolved.

Herein, one-pot spray engineering of a new design of $\text{Na}_{0.44}\text{MnO}_2$ cathode structure is investigated as a potential route to high-rate and cycle-stable SIBs. The adjustable design of the electrode from a dense to an open sponge-like structure is performed by

different concentrations of component solution during the one-pot spraying, which has been attributed to the direct layer-by-layer deposition of aggregations with size discrepancy and can effectively enhance the electrochemical kinetics and capacity for SIBs. In this study, the SIB with the open sponge-like electrode is noted to exhibit improved rate capacity compared to the dense one. The improved electrochemical performance is attributed to the unique effect of the open sponge-like structure to provide efficient and stable charge transportation within the electrode structure with short diffusion pathways and an improved specific surface area for Na ion interaction.

2. Experimental

For obtaining the $\text{Na}_{0.44}\text{MnO}_2$ active material through sol-gel method, manganese (II) acetate tetrahydrates $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$, 99.99%, Sigma, Welwyn Garden City, UK) and sodium nitrate (NaNO_3 , 99.0%, Sigma) with 0.46:1 of Na:Mn molar ratio were dissolved into deionized (DI) water with 0.1 M citric acid $(\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$, 99.5%, Sigma) acting as chelating agent. After stirring for 1 h, the transparent solution was dried at 100 °C for 12 h until all the solvent evaporated. The resultant solid precursors were ground and then heat-treated at 800 °C for 10 h to obtain $\text{Na}_{0.44}\text{MnO}_2$. The spray suspensions were prepared by dispersing $\text{Na}_{0.44}\text{MnO}_2$, carbon conductivity enhancer (Super P, MTI Corporation, US), polyvinylidene fluoride (PVDF, $M_w = 534,000$, Sigma) binder as a weight ratio of 80:10:10 into a 70:30 vol% bi-solvent mixture of acetone (99.5%, Sigma) and 1-Methyl-2-pyrrolidinone (NMP, 99.5%, Sigma) by ultrasonic treatment for 30 min. The concentration of spray suspensions was adjusted to be 0.5, 4.0, 6.0, and 8.0 g/L to design the electrode from dense to porous structures. During the spray process, a copper foil or stainless steel disc was held on a vacuum chuck set heated to 150 °C. The suspensions were atomized by compressed air (~0.3 bar) through an industrial spray nozzle attached to an *x-y-z* linear manipulator gantry to directly deposit the suspension onto a controlled area on the current collector. Any solvent of the deposited suspension was instantly evaporated, resulting in the one-pot construction of the electrodes with different structures.

The morphology of the electrode structure was investigated using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and a 3D surface confocal laser scanning microscope (3D surface CLSM, Carl Zeiss, Dresden, Germany). The machining of the electrode for cross viewing was carried out by a cross-section polisher (IB-09020CP, JEOL, Tokyo, Japan). The crystal structure was investigated using X-ray diffraction (XRD) with $\text{Cu } K_\alpha$ radiation between 10 and 80° at a step size of 0.02°. The chemical composition and bonding states were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS ultra-delay line detector equipped with an Al K_α X-ray source, Korea Basic Science Institute, KBSI, Daedeok Headquarters). The wettability of the electrode in the electrolyte was investigated using a contact angle measurement system.

The profiling of electrochemical performance was performed within coin-type half cells assembled in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm) with the prepared electrode as the cathode, a Na metal foil as the anode, a glass microfiber filter (GF/F, Whatman) as the separator, and a 1.0 M NaClO_4 solution in a 1:1 vol.% mixture of ethylene carbonate (EC) and propylene carbonate (PC) as the electrolyte. The loading and packing density of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes were obtained by comparing the weight and thickness before and after the deposited layer. Galvanostatic charging/discharging was performed between 1.5 and 4.3 V at different current conditions (1 C-rate = 120 mA/g), rate capability was investigated at varying C-rates of 0.1, 0.2, 0.5, 1, 2, and 5 C, and the cycling retention was analyzed up to 100 cycles at a high 5 C-rate, all using an Arbin cycler system (Arbin BT-G-25) at room temperature. Cyclic voltammetry was performed at a range of scan rates of 0.1, 0.5, and 1 mV/s and electrochemical impedance spectroscopy (EIS) for the fresh and cycled (100 cycles) electrodes was carried out with an amplitude of 5 mV in the frequency range from 10^5 to 10^{-2} Hz, both using an Autolab system (Metrohm) at room temperature. The

energy density (E , Wh/kg) and power density (P , W/kg) are calculated using galvanostatic charging/discharging tests, as using the following Equations (1) and (2) [1,4]:

$$E = \frac{1}{m} \int_0^t V(t) \cdot I \cdot dt \quad (1)$$

$$P = \frac{E}{dt} \quad (2)$$

where m is the weight of active material, V is the discharging voltage, I is the current density, and dt is the total discharge time.

3. Results and Discussion

Figure 1a–d shows the different electrode surfaces by varying the solution concentrations during the one-pot spraying process. Using the 0.5 g/L solution concentration (Figure 1a), the construction of a dense electrode structure was observed. Increasing the solution concentration to 6.0 g/L forms a porous network surface with an increased average pore size from 12.5 μm for 4.0 g/L (Figure 1b,i) to 23.7 μm for 6.0 g/L (Figure 1c) due to the interconnected agglomerates of the $\text{Na}_{0.44}\text{MnO}_2$ nanorods (see Figure S1a). Figure 1i shows that at the same mass loading, as the solution concentration increases from 0.5 to 6 g/L, the packing density decreases until it becomes stable at 6 g/L. For a series of cross-section SEM images (Figure 1e–h), increasing solution concentration for spraying shows that the 6.0 g/L electrode has the same thickness as the 8.0 g/L electrode, indicating that an open sponge-like structure was constructed by the extension of the pores between the interconnected solid framework in the overall area from the surface into the current collector. For 8 g/L and above electrodes, the uneven structure is formed by the deposition of irregular agglomerates following the decrease of the measured thickness and pore size on the electrode structure, which does not have the benefit of an open sponge-like structure for the electrochemical reactions. There is no critical variation of the crystal structure of the $\text{Na}_{0.44}\text{MnO}_2$ active material among the electrodes fabricated using the different solution concentrations, as indicated by emitted diffraction peaks of (130), (140), (200), and (360) at 13.96, 16.68, and 19.45, and 35.92°, respectively, indicating the orthorhombic structure with *Pbam* space group (JCPDS No. 27-0750) (Figure 1j) and the balanced intensity ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ (intensity ratio 1) calculated from the Mn 2p spectra (see Figure S1b) [42,43].

The mechanism of the $\text{Na}_{0.44}\text{MnO}_2$ electrode structure adjustment from dense to open sponge-like structures by one-pot spraying can be attributed to the stacking behavior of the solid component during layer-by-layer deposition of the suspension. During spraying (Figure 2a), the spray nozzle atomizes the suspension into numerous micro-droplets which tend to form aggregations as a result of drying in the vicinity of the heated substrate [25]. The concentration of the suspension is a major factor in determining the degree of aggregate, affecting the resultant aggregation size [44]. For low-concentration suspensions, the solid components induced from spread droplets were stacked up one by one neatly, resulting in a dense electrode structure by filling the sprayed components in the empty space by the layer-by-layer deposition, as confirmed by the SEM images of the electrodes with increasing mass loadings using the same suspension concentration of 0.5 g/L (Figure S2a–c). The fully filled body (EDS mapping of Mn element in the cross-section of the 0.5 g/L electrode, see Figure 2b) and smooth surface (line profile of 3D surface CLSM, Figure 2c,d) were clearly observed in the electrode structure. On the other hand, a high concentration suspension could limit the spreading of the droplets, leading to the enlargement of the resultant aggregation sizes (EDS mapping of Mn element in the cross-section of the 6.0 g/L electrode, see Figure 2e). Hence, during the gradual stacking of the solid component on the current collector (Figure S2d–f), the enlarged aggregations lead to the formation of the vacant areas between them from the bottom to the top of the electrode (see Figure 2e) due to the heterogeneous interlocking of the deposited product (Figure 2f,g), leading to the construction of free pathway networks for electrolyte penetration and an adequate

surface area to accommodate violent structural deformation of the electrode induced by the electrochemical reactions of the Na ions [45].

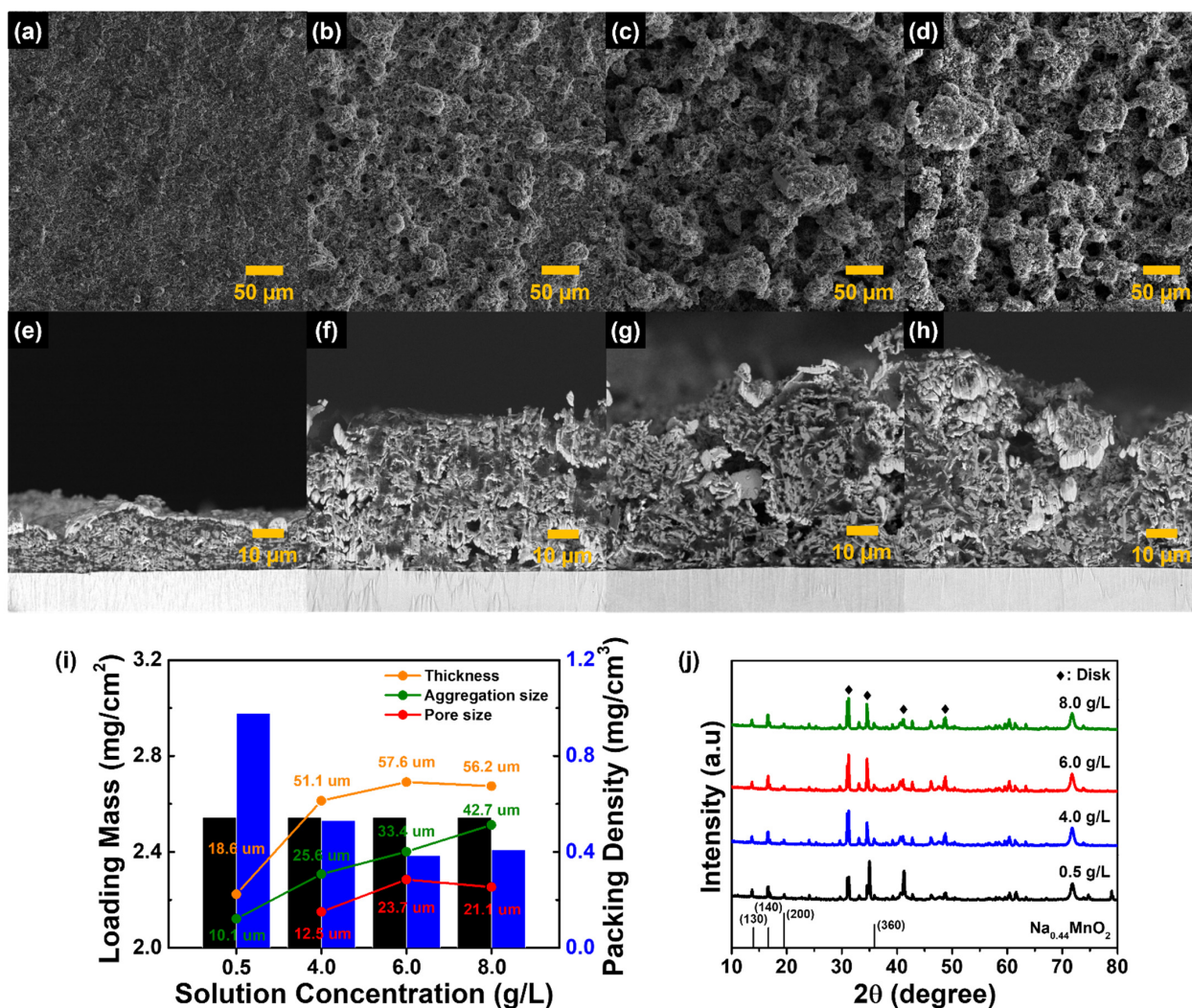


Figure 1. (a–d) Surface-view and (e–h) cross-section SEM images of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes with increasing solution concentrations from 0.5 to 8.0 g/L fabricated by the one-pot spraying process, (i) comparison of the electrode factors (loading mass (black histogram), packing density (blue histogram), thickness, aggregation size, and pore size) with the varying solution concentrations, and (j) the XRD curves of all the electrodes.

The galvanostatic charge/discharge voltage profiles measured at 0.1 C expose a difference in the electrochemical behavior among the electrodes (Figure 3a). Compared to the dense electrode structure made by the suspension concentration of 0.5 g/L, the charge/discharge profiles of the electrodes made by the higher suspension concentrations show six more distinct plateaus, indicating the consecutive phase transitions of $\text{Na}_{0.44}\text{MnO}_2$ during Na-ion intercalation and deintercalation [46], especially for the electrode made by the suspension concentration of 6.0 g/L, resulting in the maximum of the initial discharge capacity (121.6 mAh/g). This is attributed to the open channels within the electrode providing an effective surface area for the electrochemical reactions of the Na ions with the $\text{Na}_{0.44}\text{MnO}_2$ active material [32]. Furthermore, as shown in Figure 3b,d, while the 0.5 g/L electrode shows rapid degradation of the specific capacity at the accelerated current densities from 0.1 to 10 C, the 6.0 g/L electrode exhibited superior capacity value and capacity retention at increasing C rates to 10 C. The 6.0 g/L electrode also exhibited higher volumetric capacities at 1 C and higher rates (Figure 3c), which can be attributed to the improved

anodic diffusion coefficient of the Na ion (D , cm^2/s , Figure 3e) that is derived by a linear relation based on peak current (I_p , mA) and scan rate (v) based on the Randles–Sevcik equation (Equation (3)) from the cyclic voltammograms in Figure S4, as follows: [47,48]

$$\frac{I_p}{m} = 0.4463 \left(\frac{F}{RT} \right)^{1/2} AD^{1/2} C v^{1/2} \quad (3)$$

where m is the electrode mass, F is the Faraday constant (96,486 C/mol), R is the gas constant (8.314 J/mol K), T is the temperature, A is the electrode area per unit mass (in cm^2/g), and C is the Na-ion concentration of the electrodes. The D values of the charging and discharging processes increased from the 0.5 g/L electrode to the 6.0 g/L electrode and then descended for the 8.0 g/L electrode (see Figure 3e and Table S1), which indicates that the open sponge-like structures tend to promote efficient delivery of Na ions to the $\text{Na}_{0.44}\text{MnO}_2$ active materials. In addition, the 6.0 g/L electrode (117.0 Ω) showed a decreased charge transfer resistance (R_{ct}) as reflected from the smaller semicircle in the high medium-frequency region in the electrochemical impedance spectroscopy (EIS) spectra (see Figure 3f) when compared to the other electrodes (564.0 Ω for the 0.5 g/L electrode, 301.5 Ω for the 4.0 g/L electrode, and 222.3 Ω for the 8.0 g/L and 390.3–1000.22 Ω in the literature for slurry coated electrodes [49–51]), which also indicates excellent charge transfer ability for the open sponge-like structures. This can prove to relax resistance for transporting both Na ions and electrons within the electrode [52]. Figure 3g,h shows that the 6.0 g/L electrode exhibited the highest gravimetric energy and power densities at all C rates and the highest volumetric energy and power densities above 1 C, demonstrating its benefits, particularly at faster C rates.

Figure 4a shows the superior cycling capability of the 6.0 g/L cathode compared with the 0.5 g/L electrode at 0.1 C for 10 cycles and then at a high rate of 5 C for 90 cycles. After 100 cycles, the 6.0 g/L electrode maintained a specific capacity value of 100.1 mAh/g (90.2% cycling retention) despite the high C-rate (5 C), whereas the capacity of the 0.5 g/L electrode considerably degraded to 32.5 mAh/g (34% cycling retention). The corresponding volumetric capacities are shown in Figure S3, showing doubling volumetric capacity for the 6.0 g/L cathode at 5 C after 100 cycles. The stable high-rate electrochemical behavior of the 6.0 g/L electrode is attributed to the unique structure that provides an efficient pathway to access and accept abundant Na ions in the high-rate electrochemical reactions [46]. This corroborates the excellent electrochemical kinetic properties shown by the highest Na-ion diffusion coefficient D and lowest R_{ct} of the EIS spectra (see Figure 3e). In order to further investigate the unique effect of the open-pores networking structure on Na storage behavior at the electrochemical reaction, we carried out the calculation of the degree of capacitive effect of the electrodes via the relationship between measured current (i) and scan rate (v) of the CV curves ($i = av^b$, where a and b are constants) [53,54]. In Figure 4b, the gradient of the $\log i - \log v$ plot deducts the b value depending on the applied voltage to indicate the proportion of capacitance-controlled behavior, as shown in the detailed value in Figure S5. The b value determined from the gradient of the $\log i - \log v$ plot is in the range between 0.5 and 1.0, where $b = 0.5$ indicates a diffusion-controlled behavior and $b = 1$ indicates a capacitance-controlled process. That is, the larger the b value, the greater the contribution of the faster surface redox reaction during charging/discharging [55]. It is noted that the b values of the 6.0 g/L electrode at the specific voltages generating the electrochemical reactions between the Na ions and electron electrode are higher than those of the 0.5 g/L electrode, which can mean generating more profound capacitive kinetics for the Na storage [56]. In the CV curve of the 6.0 g/L electrode at 0.5 mV/s (Figure 4c), there are six main pairs of redox peaks indicating the charge ordering during the electrochemical behavior of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes [5,11] (the other CV curves for both 0.5 g/L and 6.0 g/L electrodes at various scan rates (v) of 0.1, 0.5, and 1 mV/s are shown in Figure S4). We also obtained the quantification of ion diffusion and surface induced capacitance contributions for each of the peaks from the CV curve. It revealed two parts of the surface

induced capacitive (k_1v) and ion diffusion-controlled intercalation ($k_2v^{1/2}$) contributions for each of the peaks by using the following equation (Equation (4)) [57,58]:

$$i(V) = k_1v + k_2v^{1/2} \quad (4)$$

or

$$i(V)/v^{1/2} = k_1/v^{1/2} + k_2 \quad (5)$$

Equation (5) means that k_1 and k_2 can be obtained from the slope and intercept, respectively, of a linear plot of $i(V)/v^{1/2}$ versus $v^{1/2}$. The plot (Figure 4d) for the qualitative comparison between the electrodes shows that the capacitive contribution is gradually improved with increasing the scan rate, which is attributed to the capacitive mechanism based on insertion/extraction of Na ions as a main factor affecting the electrochemical reactions of the electrodes [59]. Interestingly, the capacitive contribution of the 6.0 g/L electrode is higher than that of the 0.5 g/L electrode at overall scan rates. This indicates that the efficient charge transportation via the open-pores networking electrode structure activates the short diffusion pathway and improves the specific surface area of the composite $\text{Na}_{0.44}\text{MnO}_2$ active materials, which is attributed to the improved wettability of the porous structure with the electrolytes, as confirmed by the wettability test where the contact angle is reduced from 112.3 to 60.3° (Figure 4e,f).

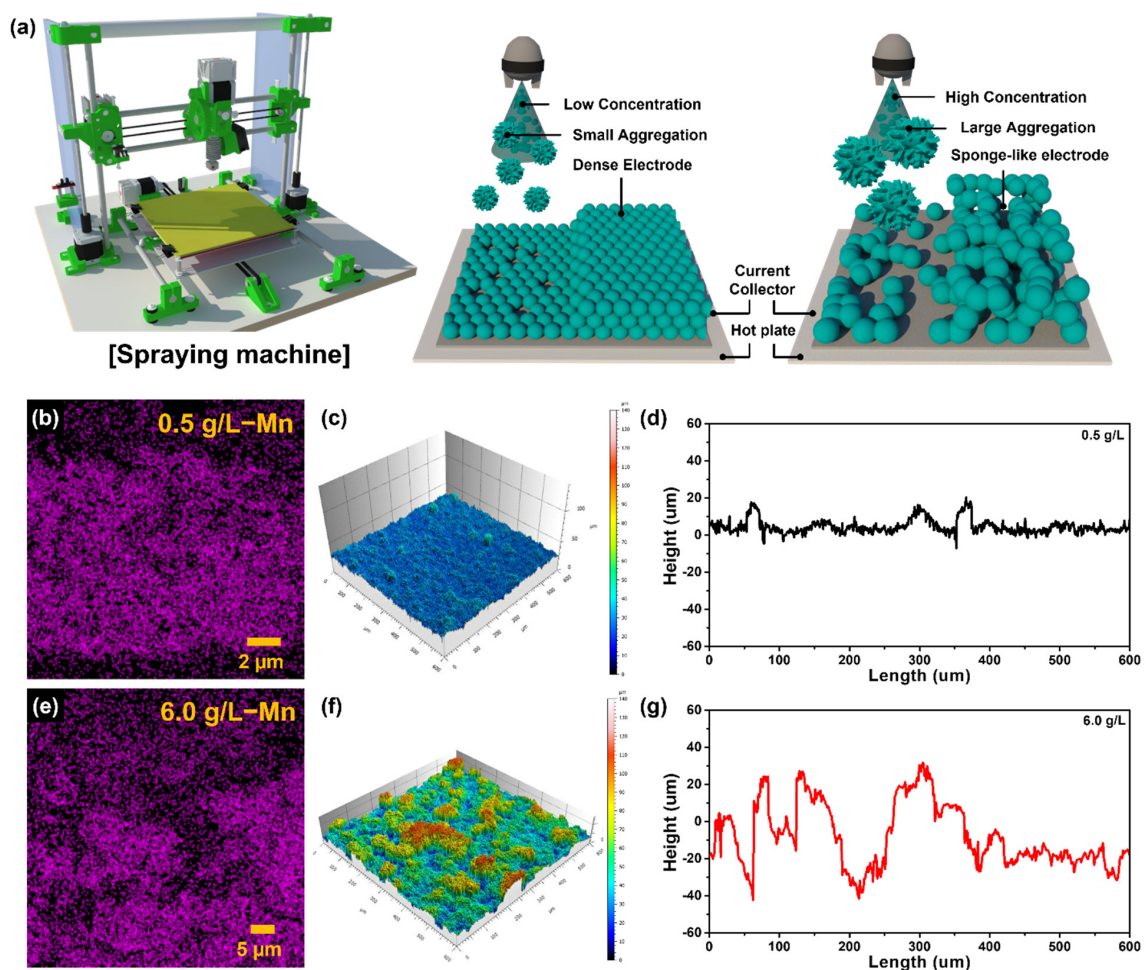


Figure 2. (a) Schematic mechanism of controllable engineering the $\text{Na}_{0.44}\text{MnO}_2$ electrode structure using different suspension concentrations during the one-pot spraying process, the EDS images of Mn element to visualize the cross section of electrode structures ((b) 0.5 g/L electrode and (e) 6.0 g/L electrode), and the 3D surface images and the resultant height plots of (c,d) 0.5 g/L electrode and (f,g) 6.0 g/L electrode using 3D surface confocal laser scanning microscope.

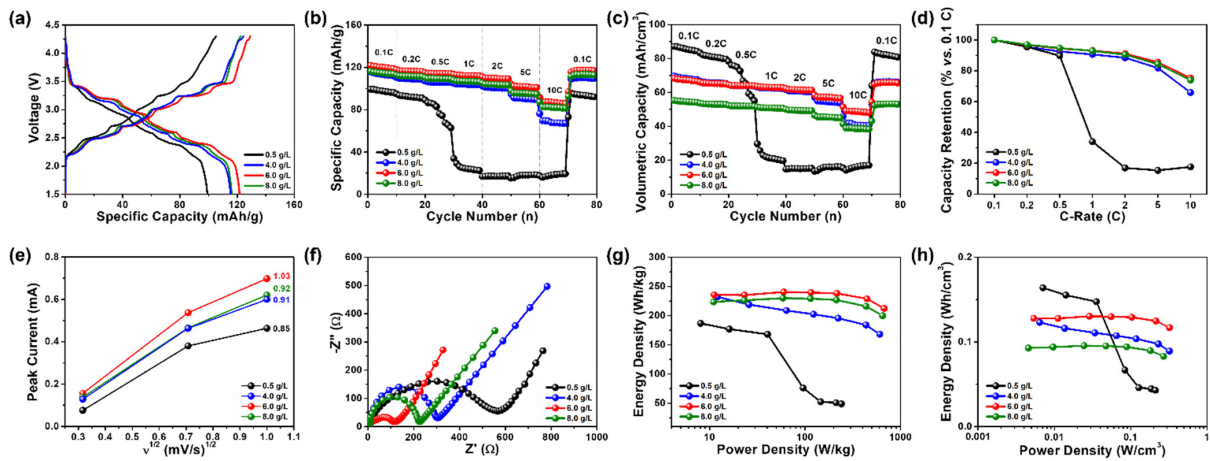


Figure 3. (a) The galvanostatic charge/discharge voltage profiles measured in range of 1.5–4.3 V at 0.1 C, (b) rate capability in (b) specific and (c) volumetric capacities, (d) plot of capacity retention in increased C-rate conditions, (e) relationship of peak current density with respect to the varied scan rates for the electrodes made by 0.5 g/L and 6.0 g/L suspension concentrations during cathodic and anodic reactions, (f) EIS spectra and curves showing the energy and power densities of the SIB cells in (g) the specific and (h) volumetric conditions.

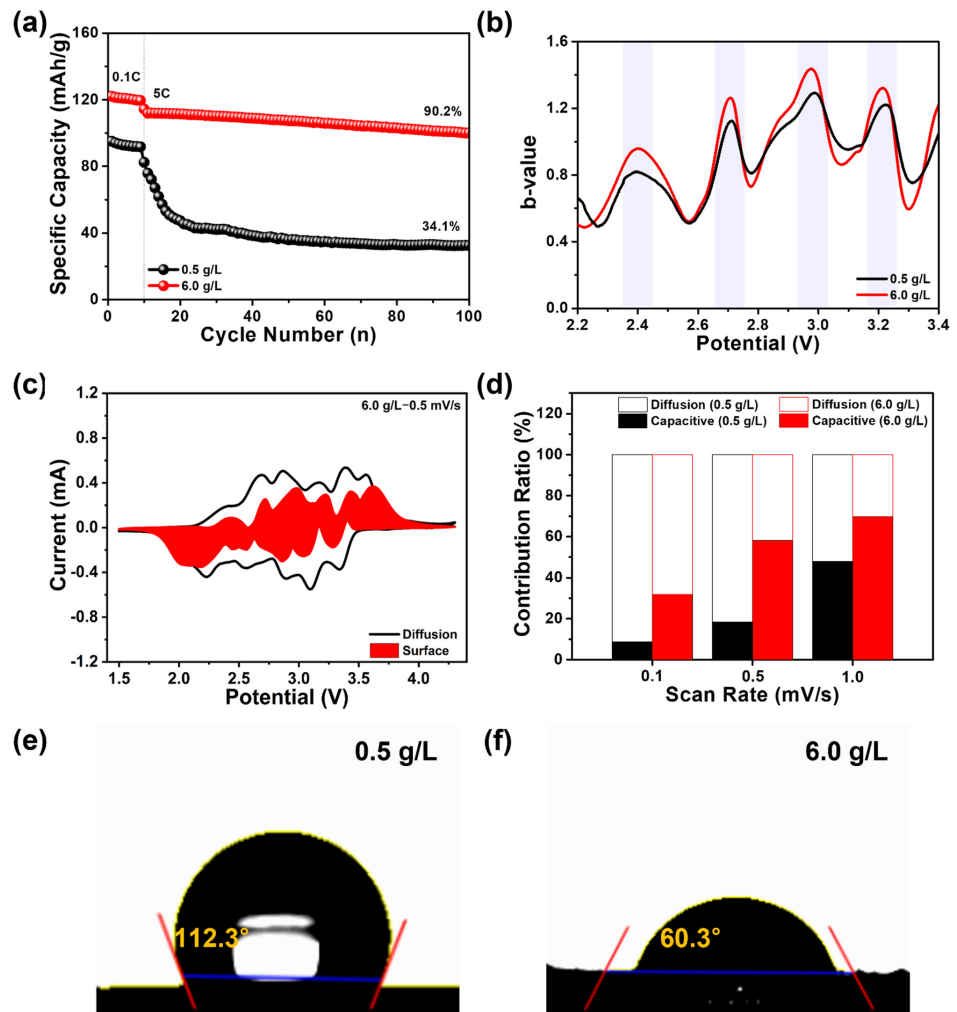


Figure 4. (a) high-rate cycling capability; (b) continuous b-value measured in potential range from 2.2 to 3.4 V along the cathodic scan; (c) CV curves of the 6.0 g/L electrode at 0.5 mV/s; each characteristic

peak has the ion diffusion and surface induced capacitance contributions; (d) the quantification of ion diffusion and surface induced capacitance of the electrodes from the CV curves; and the visual results of wetting angle between the electrolyte and electrode surface; ((e) 0.5 g/L electrode; and (f) 6.0 g/L electrode).

To better understand the design role of the $\text{Na}_{0.44}\text{MnO}_2$ electrode structure on the high-rate cycling capability of the SIBs, ex situ XRD was used to trace the electrochemical behavior of the Na ions after cycling from the lattice [60,61]. In Figure 5a, the patterns of the 0.5 g/L electrode after 100 cycles between 1.5 and 4.3 V at the 5 C-rate show a shift of the diffraction peaks toward larger 2θ values from 1.5 to 4.3 V [62]. There was a larger peak shift for the 6.0 g/L electrode (Figure 5b) than the 0.5 g/L electrode. This is in agreement with the Mn 2p XPS result showing peaks relating to the Mn ions for the 6.0 g/L electrode, whereas the Mn 2p spectrum of the 0.5 g/L electrode does not show obvious peaks due to excessive emergence of irreversible Na-related compounds (Figure S6). The reversible processes in the crystal structure (see ex situ XRD) and chemical bonds (see XPS) are expected to follow the soft movement of sodium ions and electrons. That is, the observed difference in the electrochemical behavior can be linked to the internal resistance of the electrodes. The EIS plot in Figure 5c,d shows that R_{ct} increased much more significantly for the 0.5 g/L electrode and at a faster C rate compared with the 6.0 g/L electrode, indicating increasing internal resistance during the extraction/insertion of the Na ions, resulting in obsolete cycling capacity due to the serious deformation of the electrode structure induced by component condensation, as shown in the SEM images of the post-mortem electrodes in Figure 5e,f [63]. In contrast, the SEM images in Figure 5g,h show that the structure of the 6.0 g/L electrode is maintained, ensuring the realization of superb high-rate and cycle-stable capabilities for SIBs.

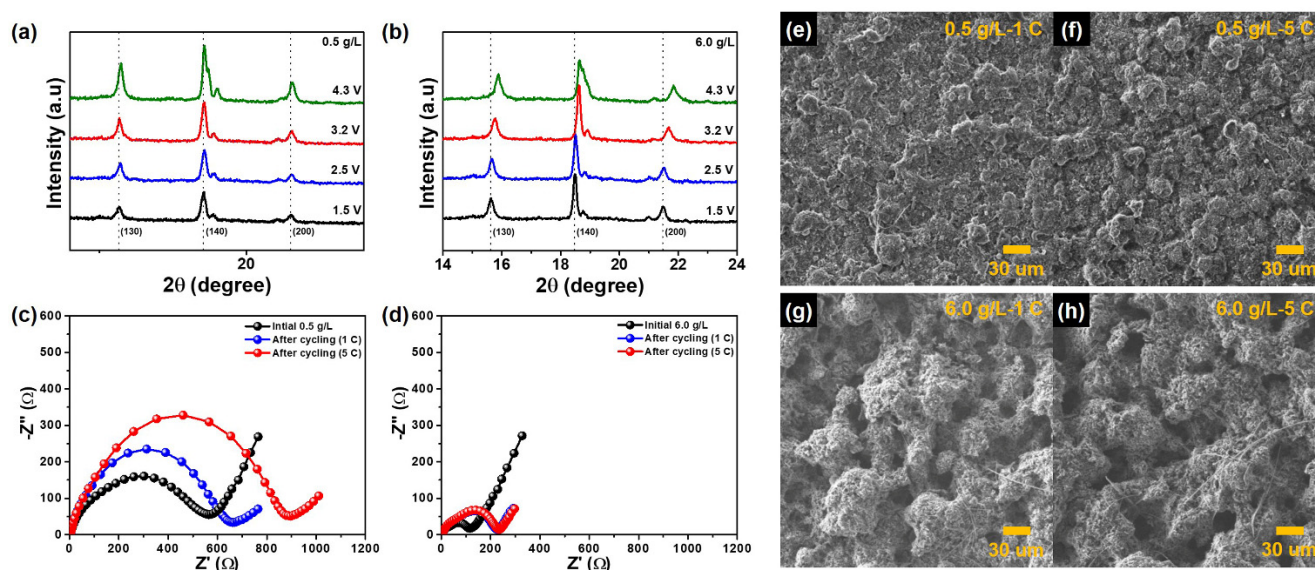


Figure 5. Ex situ XRD results of (a) 0.5 g/L electrode and (b) 6.0 g/L electrode, EIS Nyquist plot after 100 cycles at 1 and 5 C-rate for (c) 0.5 g/L electrode and (d) 6.0 g/L electrode, and the resultant SEM images after high-rate cycling measurement (e,g) 0.5 g/L electrode and (f,h) 6.0 g/L electrode).

4. Conclusions

A cathode material of $\text{Na}_{0.44}\text{MnO}_2$ was synthesized, and a unique open sponge-like cathode structure was fabricated via controlled engineering of a one-pot spraying process for Na-ion batteries. The one-pot spraying process directly adjusts the electrode structures from dense to porous by adjusting the spraying suspension concentration. The critical suspension concentration (6.0 g/L) drives the direct layer-by-layer deposition of enlarged aggregations on the substrate to make the electrode structure with the vacant areas ranging from bottom to top. As a result, the open sponge-like electrode structure

realizes higher specific capacity, rate capability, and capacity retention compared to the dense electrode (0.5 g/L), which can be induced by the improved diffusion coefficient and enriched electroactive sites in the electrochemical reactions of the Na ions with the electrode interfaces. In addition, the high-rate cycling capability of the open sponge-like electrode is noted in both the specific (100.1 mAh/g and 90.2% cycling retention after 100 cycles at 5 C). The superior electrochemical performance is attributed to the efficient and stable charge transportation via the open-pores networking electrode structure for providing the shortened diffusion pathway and improved specific surface area to the composite Na_{0.44}MnO₂ electrode. The Na_{0.44}MnO₂ active material exhibits reversible phase transition during the high-rate electrochemical reaction with Na ions as shown in the ex situ XRD. Additionally, the electrode structure is maintained over cycling as a result of maintaining the low internal resistance of the electrodes in the condition of increasing C-rate. To the best of the present authors' knowledge, this is the first report on the unique design of the cathode electrodes with superior high-rate capabilities of the SIBs through the one-pot spraying process, and we believe that one-pot spray engineering can be utilized as a potential milestone to boost the development of advanced structures for high-rate and cycle-stable SIBs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries8100181/s1>.

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