## RESEARCH ARTICLE



# Carbon quantum dot-laminated stepped porous Al current collector for stable and ultrafast lithium-ion batteries

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### Funding information

Ministry of Science and ICT(MSIT), Korea, Grant/Award Number: 2021COMPA-106; National Research Foundation of Korea. Grant/Award Number: NRF-2021R1A6A1A03039981

## Summary

Designing an interfacial architecture between the current collector and electrode plays a serious role in developing the specific capacity with cycling stability of lithium-ion batteries (LIBs). Consequently, an original approach to enhance the structure of the interface between the current collector and electrode is necessary. Thus, we developed a novel interface architecture based on carbon quantum dots (CQDs)-laminated on a stepped porous Al (SP-Al) current collector to attain stable and ultrafast-discharge LIBs and CQD-SP-Al for application as LIB cathodes. To this end, the electrochemical etching and ultrasonic spray coating methods were employed. The cathode assembled with CQD-SP-Al displayed the adhesion enhancing, an increased redox reaction kinetics, and the magnificent interfacial stability of the current collector//electrode interface because of the increased surface roughness, stepped pores with N-doped CQD, and uniform CQD lamination layer. The resultant cathode with CQD-SP-Al showed an enhanced specific capacity of 78.2 mAh/g and capacity retention of 92.6% at a high C-rate of 10C after 500 cycles. This great cycling stability is due to an expanded interfacial contact area of current collector// electrode with improved adhesion, as well as to the CQD lamination layer, while the excellent ultrafast discharge capacity is ascribed to the risen number of charge supplying/collecting sites, the stepped porous structure, and the highly conductive N-doped CQD lamination layer.

### KEYWORDS

cathode, current collector, electrochemical etching, interfacial coating layer, lithium-ion batteries

#### **INTRODUCTION** 1

Because of the excellent energy density, large operating voltage window, and environment-friendly, lithium-ion batteries (LIBs) have been extensively used as the power supply of many electric devices, like smart phones, drones, laptops, tablets, and electric vehicles.<sup>1,2</sup> However, despite their frequent use in electronic devices, LIBs even now have critical issues including poor cycling stability, low discharge capacity, and slow charging speed, which limit their application in advanced electrical devices. Some companies are aiming to develop electric vehicle batteries, that can be completely charged within 6 minutes, requiring the charging speed faster than the C-rate of 10C.<sup>3-6</sup> Under ultrafast-charging conditions, there are many problems such as a drastically reduced lifetime and risk of explosion. Among the various causes of these problems, unstable interfacial conditions, such as those at the active material//additive, electrode//electrolyte, and current collector//electrode interfaces, are

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important factors to be considered. In particular, during ultrafast charging, the problems linked to the interface of electrode//current collector are exacerbated, resulting in decreased cycling stability with specific capacity of LIBs. These problems are related to the limited redox reaction rates of electrons and Li<sup>+</sup> ions, exfoliation of the electrode at the current collector by a volume dilatation, and dissolution of active materials, with corrosion of the current collector.7,8

To overcome these problems, interfacial engineering is crucial strategy used to enhance the mechanical, electrochemical, and chemical stabilities of LIBs by designing a geometrical structure of interfaces. In terms of active materials, various studies have been conducted to prevent volume expansion, dissolution, and unstable surface reactions using the surface coating method (eg, LiAlO<sub>2</sub> coated LMO,<sup>9</sup> NB-doped TiO<sub>2</sub> coated LMO,<sup>10</sup> Li<sub>2</sub>CO<sub>3</sub>/LiNbO<sub>3</sub> coated NCM622,<sup>11</sup> and LiAlO<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub> coated NCA<sup>12</sup>). However, despite the improved surface properties of the active materials, an exfoliation of the electrode at the surface of the current collector remains a grave problem. Therefore, to attain the ultrafast cycling performance with stability, a unique engineering of interface which can improve the interface of current collector//electrode is necessary for stable and ultrafast LIBs.

Herein, we propose a unique interfacial structure for an N-doped carbon quantum dot (CQD) coated stepped porous Al foil (COD-SP-Al) that can be employed as a current collector for LIB cathodes; further, we demonstrated the effects of the novel interfacial architecture for the ultrafast cycling performance of LIBs. The stepped porous interfacial structure successfully improved the interfacial contact area of electrode//current collector due to the increased surface roughness. Owing to the advantages of a small particle size and increased surface functional groups, the CQDs can be more uniformly laminated compared with other carbon-based coating materials, like carbon nanotubes or graphene.<sup>4,13</sup> The ultrasonic spray coating method also has additional merits, such as simplicity, a low cost, and reproducibility. In particular, the ultrasonic vibration of spraying nozzle generates fine precursor droplets, enabling the formation of a more uniform coating layer on a complex surface when compared with other coating methods such as dip or conventional spray coating.<sup>14,15</sup>

#### **EXPERIMENTAL** 2

A stepped porous Al foil was well fabricated via electrochemical etching. To develop the stepped porous interfacial structure, pristine Al foil (99.9%, thickness of 15 µm) was electrochemically etched in a blended solution of 0.1 M hydrochloric acid (HCl, 37%), 0.29 M nitric acid

(HNO<sub>3</sub>, 70%), and 0.16 M hydrofluoric acid (HF, 53%) in deionized water. The electrochemical etching procedure was conducted utilizing the potentiostat/galvanostat (PGSTAT302N, Metrohm) on a three-electrode system, which consisted of pristine Al foil Pt wire, and Ag/AGCl (saturated in KCl) as a working electrode, a counter electrode, and reference electrode, respectively. For the electrochemical etching, the voltage was kept at 0.4 V during 180 seconds to form a stepped porous surface of the Al foil.

The CQDs were synthesized using hydrothermal treatment, centrifugation, and dialysis. Specifically, 2.73 g of citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, 99.5%, Aldrich) and 1.24 g of urea (CH<sub>4</sub>N<sub>2</sub>O, 99.0%, Aldrich) were dispersed in 30 mL of DI water. Afterwards, the dissolved solution was transmitted to an 80 mL autoclave and reacted at 180°C during 6 hours. After cooling the autoclave, the solution was centrifuged two times for 20 minutes at 10 000 rpm and then dialyzed during 24 hours. The resultant solution was desiccated in the oven at 50°C during 24 hours to gain the CQD powder. To develop the CQD lamination layer at the surface of the stepped porous Al, an ultrasonic spray coating was conducted utilizing a 1 wt% CQD solution in NMP. For the ultrasonic spray coating, the frequency, feeding rate, spray time, and distance between the Al foil and the spray nozzle were kept at 130 kHz, 3 mL/h, 7 minutes, and 25 cm, respectively. The pristine Al foil without any other treatment, stepped porous Al foil without CQD coating, CQD-coated Al foil without electrochemical etching, and stepped porous Al foil with CQD coating are hereafter referred to as bare Al, SP-Al, CQD-Al, and CQD-SP-Al, respectively.

The morphologies and compositions of the CQDs were characterized by transmission electron microscopy (TEM, Tecnai G2, KBSI Gwangju Center), and the absorbance and chemical binding states of CQDs were measured via ultraviolet-visible (UV-vis) spectroscopy (Lambda-35) and Fourier-transform infrared (FT-IR) spectroscopy (Nicolet IS50), respectively. Furthermore, the surface morphology and roughness of bare Al, SP-Al, and CQD-SP-Al were analyzed by field-emission scanning microscopy (FESEM, Hitachi S-4800) and laser scanning microscopy (LSM, LSM 800 MAT). The crystal structures and chemical binding states of bare Al, SP-Al, and CQD-SP-Al were revealed via X-ray diffraction (XRD, D/Max-2500) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, with Al  $K_{\alpha}$  as X-ray source). Also, the thickness of CQD lamination layer was analyzed by cross-section TEM of CQD coated Al foil after focused ion beam milling system (FIB, Carl Zeiss, Crossbeam 350).

The electrochemical performance about all samples was evaluated by coin-type half cells (CR2032), which consist of a cathode with the fabricated current collectors,

a Li foil (Honjo Chemical Corp, 99.95%) anode, a porous polypropylene membrane as a separator (Celgard 2400), and a solution of 1.0 M LiPF<sub>6</sub> dissolved in a blended solvent of ethylene carbonate and dimethyl carbonate (1:1 vol%) as an electrolyte. To produce the cathode, the slurry was composed of 70 wt% of LMO (POSCO M-TECH) as the active material, 20 wt% of polyvinylidene fluoride (PVDF, Kynar 900) as a binder, and 10 wt% of ketjen black (EC600JD) as a conducting agent in NMP as a solvent. The slurry was then coated on bare Al, SP-Al, CQD-Al, and CQD-SP-Al as a current collector and dried at 100°C for 10 hours in oven. All cells were brought together in a high-purity-argon-atmosphere glove box, keeping O<sub>2</sub> and H<sub>2</sub>O consistence of fewer than 5 ppm. To determine the electrochemical kinetics and resistance of all electrodes, electrochemical impedance spectroscopy (EIS) was fulfilled in the frequency ranging from  $10^5$  to  $10^{-2}$  Hz with an AC voltage of 0.005 V. To prove the optimum stepped-porous structure, the electrochemical etching time of Al foil was controlled by 60, 180, and 300 seconds (referred to as P-Al 60s, P-Al 180s, and P-Al 300s, respectively). The FESEM of SP-Al 60s and SP-Al 300s was performed, and the C-rate performances at 1C, 3C, 5C, 7C, and 10C for 10 cycles of prepared Al foils were investigated. To evaluate the electrochemical performances of all electrodes, cycling tests were executed utilizing the battery cycler system (WMPG 3000S) in the potential ranging from 3.3 to 4.3 V (vs Li/Li<sup>+</sup>). The cycling stability were investigated up to 100 cycles at 1C (148 mA/g), and the rate performances of all electrodes were measured at assorted C-rate of 1C, 3C, 5C, 7C, and

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10C for 10 cycles. To further analyze the electrochemical reaction, the cyclic voltammetry of all electrodes was conducted in the potential range of 3.3 to 4.3 V (vs  $Li/Li^+$ ) with scan rate of 1 mV/s. Also, the ultrafast cycling performances of all electrodes were evaluated for 500 cycles at 10C. To confirm the interfacial contact area of electrode//current collector, cross-sectional FESEM images of the bare Al, SP-Al, and COD-SP-Al electrodes were observed. In addition, FESEM images about bare Al and CQD-SP-Al electrodes were obtained after cycling to investigate the interfacial stability under ultrafast cycling conditions.

#### **RESULTS AND DISCUSSION** 3

The Figure 1 shows a graphic illustration of the electrochemical etching and ultrasonic spray coating procedure of the Al foil. The stepped porous surface on the Al foil was developed via electrochemical etching utilizing a potentiostat/galvanostat in a mixed solution of HCl, HNO<sub>3</sub>, and HF, which was used as the etchant. Generally, an Al<sub>2</sub>O<sub>3</sub> layer with a thickness of about 30 to 100 Å, which has a lofty chemical/physical stability and poor electrical conductivity, is naturally developed on the face of the Al foil because of the moisture in air. Nevertheless, the Al<sub>2</sub>O<sub>3</sub> layer can be removed in the voltage ranging from -1.3 to 1.2 V using an acidic ambience with a pH under 4. In accordance with the Pourbaix diagram of the Al-H<sub>2</sub>O system, the Al<sub>2</sub>O<sub>3</sub> is in a stable  $Al^{3+}$  state in an acidic ambience with a pH under 4 at a potential of



FIGURE 1 Graphic illustration. Schematic of the electrochemical etching and ultrasonic spray coating procedure of the Al foil

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-0.5 V (vs SHE). In this condition, stepped porous structures are developed by the decomposition of  $Al^{3+}$  in an acidic condition in accordance with the following chemical reactions (see Equations (1)-(3)).<sup>16-18</sup>

$$Al + 4F^- \leftrightarrow AlF_4 + 3e$$
 (1)

$$\mathrm{Al}^{3+} + \mathrm{H}_2\mathrm{O} \leftrightarrow [\mathrm{AlOH}]^{2+} + \mathrm{H}^+ \tag{2}$$

$$[AIOH]^{2+} + NO^{3-} \leftrightarrow [AIOHNO_3]^+$$
(3)

The stepped porous structure on the surface of the Al foil can increase the contact area of electrode//current collector, which enhances interface adhesion and in turn quickens the interfacial reaction. In addition, the CQD lamination layer was pertained on the stepped porous Al foil using ultrasonic spray coating. The ultrasonic vibration of the spraying nozzle generates fine CQD droplets, enabling a uniform COD coating on the stepped porous Al foil. This uniform CQD lamination layer can provide high chemical stability by preventing the corrosion of Al foil from by-products such as HF.<sup>13</sup>

To confirm the morphology and structure of the CODs, TEM analysis was conducted as shown in

Figure 2A,B. The low-resolution TEM image in Figure 2A shows that the CQDs have an average size of  $\sim$ 4.13 nm. The high-resolution TEM image in Figure 2B implies that the CQDs have a lattice fringe spacing of 0.32 nm, that corresponding the (002) plane of graphite.<sup>19,20</sup> Applying an inverse fast Fourier transform (FFT) to the high-resolution TEM image in Figure 2C also confirms the presence of graphitic carbon.<sup>21</sup> Figure 2D shows an UV-vis absorbance spectrum with photographs of the CQD solution. While the CQD suspension on the left was dark blue with no fluorescence under day light, it fluoresced bright blue as shown on the right under UV light with a wavelength of 365 nm. The UV-vis absor-

bance spectrum of the CQDs exhibited two absorption peaks around 234 and 330 nm, corresponding to the  $\pi$ - $\pi$ \* transition of the aromatic sp<sup>2</sup> domains, including the C=C and C=N bonds, and the n- $\pi^*$  transition of  $C=0.^{22-24}$  As shown in Figure S1, the FT-IR spectrum of CQDs displayed stretching vibrational peaks at approximately 3446, 3213, 1662, 1631, 1576, 1394, and 1166 cm<sup>-1</sup>, corresponding to O–H, N/C–H, C=O, C=C, C-N, C-H, and N-H.<sup>19,25</sup> Thus, it was verified that Ndoped CODs were successfully fabricated via hydrothermal treatment utilizing urea as the nitrogen doping source.



FIGURE 2 (A, B) Low- and highresolution TEM image, (C) FFT result of CQD, and (D) UV-vis absorbance spectrum with photographs of CQD solution

Figure 3 displays the top-down (A-C) and crosssectional (D-F) FESEM images of bare Al, SP-Al, and CQD-SP-Al, respectively. In Figure 3A,D, the bare Al has a smooth surface morphology. By contrast, SP-Al (see Figure 3B,E) and CQD-SP-Al (see Figure 3C,F) have rough surface morphologies with stepped porous structures of sizes ranging from 8.4 to 14.7 µm and 7.8 to 14.29 µm, respectively. While SP-Al shows sharp stepped pores, CQD-SP-Al shows soft stepped pores on account of the presence of the CQD lamination layer. In the LSM images (see Figure S3G-I), SP-Al showed stepped pores with sizes of 7.9 to 14.8  $\mu$ m and depths of 2.3 to 8.1  $\mu$ m, and the CQD-SP-Al showed stepped pores with sizes of 7.5 to 13.9 µm and depths of 1.9 to 7.5 µm, which are coherent with the FESEM results. In addition, the ENERGY RESEARCH -WILEY

arithmetic mean height  $(S_a)$ , developed interfacial area ratio  $(S_{dr})$ , and arithmetic mean deviation of the roughness profile  $(R_a)$  are summarized in Table S1. The electrochemical etching process was shown to increase the surface roughness, indicated by the increased  $S_{a}$ ,  $S_{dr}$ , and  $R_{\rm a}$  of SP-Al (1.38  $\mu$ m, 77.2%, and 2.43  $\mu$ m) and CQD-SP-Al (1.37  $\mu$ m, 71.2%, and 2.03  $\mu$ m) when compared with those of bare Al (0.06  $\mu$ m, 2.9%, and 0.22  $\mu$ m). From these values, we concluded that the stepped pores formed on the face of the Al foil can dramatically increase the surface roughness of SP-Al and CQD-SP-Al. However, in practice, it was hard to discriminate the CQD lamination layer on CQD-SP-Al due to the patterns; therefore, we analyzed the cross-sectional TEM images of the CQDcoated Al foil without electrochemical etching, as shown



FIGURE 3 (A-C) Top-down, (D-F) cross-sectional FESEM images, and (G-I) 3D with top-view LSM images of bare al, SP-Al, and CQD-SP-Al

in Figure S2. Through these analyses, a CQD lamination layer with a uniform thickness of  $\sim$ 49.8 to 51.2 nm was found on the Al foil. From these analyses, we observed that the improvement of the interfacial contact area of electrode//current collector enhances the adhesion of SP-Al and CQD-SP-Al.<sup>3,4</sup> The CQD lamination layer can also act as a passivation layer and CQD-SP-Al exhibits improved cycling stability by suppressing the corrosion of the Al current collector, both adding to the potential benefits of CQD coatings.<sup>13</sup>

Figure 4A shows the XRD patterns of bare Al, SP-Al, and CQD-SP-Al. The all samples showed the four main diffraction peaks at  $\sim 38.5^\circ$ ,  $\sim 44.7^\circ$ ,  $\sim 65.1^\circ$ , and  $\sim 78.2^\circ$ , corresponding to the (111), (200), (220), and (311) planes of Al (JCPDS card No. 85-1327). Due to the relatively small amount of coated CQDs, the diffraction patterns of CQD in the CQD-SP-Al were not distinctly observed. Thus, XPS analysis was conducted to examine the chemical bonding state of the surface of CQD-SP-Al (see Figure 3B-D). All XPS spectra were calibrated at a C1s binding energy of  $\sim$ 284.5 eV. The C1s spectrum of the CQD-SP-Al (see Figure 4B) showed five characteristic peaks at ~283.7, ~284.5, ~285.3, ~286.4, and ~288.8 eV, corresponding to the C=C, C-C, C-O, C-N, and O-C=O

bindings, respectively.<sup>26</sup> Furthermore, in the O1s spectrum of CQD-SP-Al (see Figure 4C), four characteristic peaks were observed at  $\sim$ 530.3,  $\sim$ 531.3,  $\sim$ 532.4, and  $\sim$ 533.2 eV, corresponding to the C=O, Al-O, C-O, and H–O bonds, respectively.<sup>27,28</sup> From the C=C bonding. C– C bonding, and oxygen-containing functional groups of CQD-SP-Al, it was confirmed that the CQD layer was well coated on the COD-SP-Al surface. In Figure 4D, the N1s spectra of CQD-SP-Al shows three peaks at  $\sim$ 398.9,  $\sim$ 400.3, and 401.9 eV, which corresponded to pyridinic-N, pyrrolic-N, and graphitic-N, respectively. While graphitic-N is located at the site of substituted C atoms in C-C bonding, the pyridinic-N and pyrrolic-N are found at the edge sites of graphite. As pyridinic-N and pyrrolic-N can provide two p-electron through the aromatic  $\pi$ -system, the N-doped CQDs can enhance the electrical properties of the material.<sup>19,29</sup> Therefore, the COD lamination layer not only increases the cycling stability by suppressing the corrosion of Al, but also improves the electrical conductivity with additional charge supplying/collecting sites.

To investigate the electrochemical characteristics, we manufactured coin-type half-cells with cathodes using bare Al, SP-Al, CQD-Al, and CQD-SP-Al as current



FIGURE 4 (A) XRD patterns of bare Al, SP-Al, and CQD-SP-Al, and XPS spectra obtained from (B) C1s, (C) O1s, and (D) N1s of CQD-SP-Al

collectors with LMO. EIS was then performed to indicate the charge transfer with Li<sup>+</sup> ion diffusion kinetics using fresh cells. The Nyquist plot is made up of a semicircle and a leant line in the high- and low-frequency region, respectively. The semicircle expresses the charge transfer resistance  $(R_{ct})$ , which means that the resistance to current flow corresponds to a Faradaic reaction, and the leant line stand for the Warburg impedance, that means the Li<sup>+</sup> ion diffusion resistance at the electrode.<sup>7,30</sup> In Figure 5A, the bare Al electrode showed a large semicircle and high Warburg impedance, which implied a poor charge transfer rate due to restricted charge supplying/ collecting sites because of a lower interfacial contact area of electrode//current collector. On the contrary, the SP-Al and CQD-SP-Al electrodes displayed smaller semicircles than those of the bare Al electrode, which means that the SP-Al and CQD-SP-Al electrodes had a lower  $R_{ct}$ because of the increased number of charge supplying/ collecting sites between the current collector and electrode. Furthermore, as shown in Figure 5B, the  $R_{ct}$  and Warburg impedance of the CQD-SP-Al electrode was the lowest in the group of all electrodes. The Li<sup>+</sup> ion diffusion coefficients about all electrodes were computed by the Warburg impedance using Equations (4) and (5).<sup>26,31</sup>

$$Z_{\text{real}} = R_{\text{e}} + R_{\text{ct}} + \sigma_{\text{w}} \omega^{-1/2} \tag{4}$$

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$$D = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma_{\rm w} \tag{5}$$

where  $R_e$  and  $\sigma_w$  are the bulk resistance in a cell and the Warburg impedance coefficient, respectively. Additionally, D, R, A, T, F, and C represent the  $Li^+$  ion diffusion coefficient, gas constant, operating temperature, electrode area, number of electrons, Faraday's constant, and molar concentration of Li<sup>+</sup> ions. The Li<sup>+</sup> ion diffusion coefficients, calculated by the Warburg impedance, of the bare Al electrode, SP-Al electrode, CQD-Al electrode, and CQD-SP-Al electrode were  $7.4 \times 10^{-13}$ ,  $11.5 \times 10^{-13}$ ,  $14.2 \times 10^{-13}$ , and  $16.2 \times 10^{-13}$  cm<sup>2</sup>/s, respectively. These Nyquist plots and Li<sup>+</sup> ion diffusion coefficients about all electrodes indicate that the stepped porous interfacial structure and the highly conductive N-doped CQD lamination layer effectively enhance the electron transfer rate with Li<sup>+</sup> ion diffusion kinetics under ultrafast charging/ discharging conditions. In essence, the improved electrochemical kinetics of the CQD-SP-Al electrode can enhance Li<sup>+</sup> ion storage capability with ultrafast cycling performance.

To confirm the effect of the stepped-porous structure of Al foil, we controlled the etching time by 60, 180, and 300 s (referred to as P-Al 60s, P-Al 180s, and P-Al 300s, respectively), and conducted the FESEM of P-Al 60s and P Al 300s (as shown in Figure S3). As the etching time



**FIGURE 5** (A) Nyquist plots, (B) relationship between  $Z_{real}$  and  $\omega^{-1/2}$ , Li<sup>+</sup> diffusion coefficient of bare Al electrode, SP-Al electrode, and CQD-SP-Al electrode

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increased, the proportion of porous areas was gradually increased. Also, to confirm the electrochemical performance of porous structure, we conducted the C-rate performance at 1C, 3C, 5C, 7C, and 10C for 10 cycles of Bare Al, P-Al 60s, P-Al 180s, P-Al 300s electrodes, as shown in Figure S4. Because of the insufficient etching time, P-Al 60s electrode exhibits the lower specific capacity than P-Al 180s electrode with small porous areas. Moreover, the P-Al 300s electrode showed lower specific capacity and poor cycling stability due to the severely damaged Al foil with excessive etching time. Thus, we proved that the optimum etching time for electrochemical performance is 180 seconds. Also, to confirm the electrochemical performance, cycling stability tests of the bare Al, SP-Al, CQD-Al, and CQD-SP-Al electrodes with LMO were conducted at a diverse current density of 1C for 100 cycles (see Figure 6A). Whereas the all electrodes had a similar specific capacity at first, (bare Al electrode: 111.6 mAh/g, SP-Al electrode: 113.3 mAh/g, CQD-Al electrode: 112.3 mAh/g, and CQD-SP-Al electrode: 115.1 mAh/g), the bare Al electrode displayed the lowest specific capacity of 92.5 mAh/g with deficient capacity retention of 82.9% after 100 cycles. The inferior cycling performance of the bare Al electrode was because of the low interfacial contact area of electrode//current collector resulting in poor

interfacial stability. By contrast, the SP-Al, CQD-Al, and CQD-SP-Al electrodes displayed a higher specific capacity of 106.6 mAh/g with capacity retention of 93.2%, specific capacity of 103.9 with capacity retention of 92.6%, and 111.7 mAh/g with capacity retention of 96.4% after 100 cycles, respectively. These promising consequences are due to an increasement of contact area and charge transfer between the stepped porous interface and CQD lamination layer. Next, Figure 6B shows the C-rate performance of all electrodes at assorted current densities of 1C, 3C, 5C, 7C, and 10C for 10 cycles. The specific capacity of the bare Al electrode sharply decreased with an increase in C-rate from 1C to 10C (42.14 mAh/g at a current density of 10C). Conversely, at the high C-rate of 10C, the specific capacities of the SP-Al, CQD-Al and CQD-SP-Al electrodes were 64.6, 54.4, and 85.5 mAh/g, respectively. In addition, at a C-rate of 10C, SP-Al and CQD-SP-Al have higher capacity retentions of 57.0%, 48%, and 74.3%, respectively, compared with that of the bare Al electrode (capacity retention of 37.6%). At a low C-rate of 1C, no notable difference in specific capacities was discovered between all electrodes due to the sufficient time for Li<sup>+</sup> ion and electron transfer. Conversely, the C-rate of 10C, all electrodes showed a decreased specific capacity because of the insufficient time for Li<sup>+</sup> ion



FIGURE 6 (A) Cycling stability at C-rate of 1C for 100 cycles, (B) rate-performance at assorted C-rate of 1C, 3C, 5C, 7C, and 10C, (C) ultrafast cycling stability at 10C for 500 cycles

and electron transfer. Nevertheless, the SP-Al, CQD-Al, and CQD-SP-Al electrodes exhibited improved specific capacities at high C-rate. In particular, the CQD-SP-Al electrode showed significantly improved specific capacity because of the enhanced redox reaction kinetics resulting from the increased number of charge supplying/collecting sites together with the increased charge transfer rate. Also, the cyclic voltammetry curves of Bare Al, SP-Al, CQD-Al, and CQD-SP-Al electrodes at scan rate of 1 mV/s were measured, as shown in Figure S5A. All electrodes showed the characteristic redox peaks of LMO (oxidation peak of ~4.18 V and reduction peaks of  $\sim$ 3.82 V and  $\sim$ 4.05 V), which means that the redox reactions of LMO based electrodes were not affected by electrochemical etching and CQDs coating. Furthermore, the charge/discharge curves at C-rate of 1C, 3C, 5C, 7C, and 10C of Bare Al, SP-Al, CQD-Al, and COD-SP-Al electrodes were shown in Figure S5B-E. All electrodes had two voltage plateaus at  $\sim$ 4.05 and  $\sim$ 3.82 V on the discharge curves. As the C-rate increases, the Bare Al, SP-Al, and CQD-Al electrodes showed degraded discharge curves. However, the CQD-SP-Al electrode maintained the voltage plateaus due to the increased charge supplying/collecting sites with highly conductive N-doped COD coating layer. Furthermore, to estimate the effect of the stepped porous structure and CQD lamination layer under ultrafast cycling conditions, we performed an ultrafast cycling test at a C-rate of 10C for 500 cycles. The bare Al electrode showed a poor specific capacity of 18.0 mAh/g with a low capacity retention of 42.4% after 500 cycles. However, the SP-Al electrode and CQD-Al electrode exhibited a higher specific capacity of 50.1 and 46.8 mAh/g with a capacity retention of 78.6% and 86.8%, respectively. The COD-SP-Al electrode exhibited an

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even further increased specific capacity of 78.2 mAh/g with a superior capacity retention of 92.6%. To verify the effect of the stepped pores and CQD lamination layer, the FESEM images of bare Al electrode and CQD-SP-Al electrode were observed after 500 cycles at C-rate of 10C (see Figure S6). Before ultrafast cycling test, the bare Al electrode and CQD-SP-Al electrode represented a smooth surface state. However, after 500 cycles at ultrafast C-rate of 10C, the surface of bare Al electrode was harmed as surface crack arisen from electrode peeling by volume expansion of electrode and exfoliation due to corrosion of current collector by the by-product from electrochemical reaction, such as HF (see Figure S6B,C), resulting in sharply decreased specific capacity. In contrast, the CQD-SP-Al electrode maintained the smooth surface similar as initial state after 500 cycles at ultrafast cycling condition and contacted interface of electrode// current collector (see Figure S6E,F). Owing to the CQD lamination layer, which can well prevent the corrosion of Al foil by HF, the CQD-SP-Al electrode exhibited an excellent specific capacity with superior capacity retention after ultrafast cycling.

Therefore, an enhanced ultrafast cycling performance for a CQD-SP-Al electrode was obtained by using a stepped porous Al foil with a COD lamination layer. The improvement in cycling stability with ultrafast cycling performance can result from the following factors (see Figure 7): (a) the increased interfacial contact area of electrode//current collector with enhanced adhesion, and the COD lamination layer, which prohibited the corrosion of the Al current collector; and (b) the increased charge supplying/collecting sites due to the stepped porous surface morphology and the highly conductive N-doped COD lamination layer of the COD-SP-Al electrode.



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## 4 | CONCLUSIONS

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In this article, we propose a stepped porous Al foil with a CQD lamination layer, fabricated utilizing electrochemical etching and ultrasonic spray coating, for application as the current collector in ultrafast LIBs. This strategy provides synergistic effects, such as the enhancement of the electrochemical kinetics and ultrafast cycling performance. CQD-SP-Al possesses a stepped porous structure with a pore size of 7.5 to 14.29 µm and depth of 1.9 to 7.5 µm, as well as a uniform CQD lamination layer with a thickness of 49.8 to 51.2 nm. Due to the novel interface structure, the CQD-SP-Al electrode showed an supplemented Li<sup>+</sup> ion diffusion coefficient  $(16.2 \times 10^{-13} \text{ cm}^2/\text{s})$ , and an great cycling stability of 111.7 mAh/g with a capacity retention of 93.2% after 100 cycles at a C-rate of 1C. additionally, under ultrafast cycling conditions at a C-rate of 10C, the CQD-SP-Al electrode showed an outstanding specific capacity of 78.2 mAh/g and cycling stability with a capacity retention of 92.6% after 500 cycles. These results were due to the following effects of the stepped porous Al foil and the CQD lamination layer. First, the enhanced cycling stability was ascribed to the increased interfacial contact area of electrode//current collector with the COD lamination layer. Second, the improved ultrafast specific capacity was attributed to the stepped porous structure with a highly conductive N-doped COD lamination layer. In conclusion, the surface engineering of Al foil with a stepped porous structure and CQD lamination layer is a promising strategy for developing current collectors for stable and ultrafast LIBs.

## ACKNOWLEDGEMENTS

This research was supported by the Commercialization Promotion Agency for R&D Outcomes(COMPA) funded by the Ministry of Science and ICT (MSIT) (Mass production technology of 4000 cm<sup>2</sup> scale carbon-coated metal components, 2021COMPA-106) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2021R1A6A1A03039981).

## DATA AVAILABILITY STATEMENT

Data available in article supplementary material

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## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

**How to cite this article:** Sung K-W, Kim K-H, Ahn H-J. Carbon quantum dot-laminated stepped porous Al current collector for stable and ultrafast lithium-ion batteries. *Int J Energy Res.* 2022;1-11. doi:10.1002/er.7776