Atomic-scale manipulation of electrode surface to construct extremely stable high-performance sodium ion capacitor

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ABSTRACT

A state-of-the-art approach has been performed to stabilize the surface of P2-type \((\text{Na}_{0.66}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2)\) (NMNC) material through the atomic layer deposition (ALD) of \(\alpha\text{Al}_2\text{O}_3\) (10 ALD cycles) to fabricate a 3 V sodium ion capacitor (NIC) with ultrahigh rate stability. This is the first known report of stabilizing the NIC electrode surface by a metal oxide coating using ALD. The capacitor constructed with an \(\alpha\text{Al}_2\text{O}_3\)-coated NMNC (NMNC-Al) cathode and a commercial activated carbon (CAC) anode in an organic electrolyte delivers a discharge capacitance of 68 F g\(^{-1}\) at 0.35 A g\(^{-1}\) current density and exhibits extremely high electrochemical stability of ~ 98% of its initial value after 10,000 cycles. In contrast, the capacitor containing a pristine NMNC electrode displays a capacity retention of 78%. The NMNC-Al/CAC cell also has an energy density of 63 Wh kg\(^{-1}\) at a power density of 6.6 kWh kg\(^{-1}\). The capacitance, energy, and power densities obtained from the NMNC-Al/CAC cell are the best-reported values for sodium-based capacitors and outperforms well-established lithium ion capacitors. The electrochemical impedance spectroscopy study reveals that the sluggish reaction kinetics of the NMNC electrode at high current density is successfully overcome by coating an ultrathin \(\alpha\text{Al}_2\text{O}_3\) layer by ALD on its surface.

1. Introduction

Atomic layer deposition (ALD) has recently received much attention as a potential candidate to develop ultrathin metal oxide coatings from a vapour phase reaction [1,2]. ALD controls the coating thickness at the angstrom level through continuous self-limiting reactions [3]. In addition, ALD offers the deposition of tunable metal films with high purity and aspect ratio, establishing ALD as a powerful technique for numerous practical applications [1–4]. The conformality of deposited films is a crucial factor for ALD over other deposition methods such as chemical vapour deposition or sputtering [1,3,5]. ALD is commonly being used to deposit Cu films for semiconductors, grow high-quality dielectrics, fabricate trench capacitors for dynamic random-access memory, and to fabricate numerous nanodevices [6,7].

The adaptability of ALD in energy storage devices and catalyst development has been widely studied and reported elsewhere [5,8]. Initially, Badot and co-workers demonstrated the fabrication and use of \(\text{V}_2\text{O}_5\) as a cathode in lithium ion batteries (LIB) [9]. Subsequently, extensive investigations on ALD for LIB were carried out and the utilization of ALD was extended to lithium-sulphur batteries, metal-air batteries, supercapacitors, and fuel cells [1,5,8–13,14]. Generally, the key application of ALD for energy storage devices contains two major features: the surface modification of electrode materials and the design of battery components not limited to the cathode, anode and separator [8,11,12]. The former is required to stabilize the electrode and electrolyte interfacial layer (EEI) to increase the lifespan of the device whereas the latter is applied to attain high electrochemical performance [12]. Unlike an inactive carbon coating, the presence of an ultrathin metal oxide layer not only prevents unwanted side reactions with the electrolyte but also enhances the discharge capacity of the cell [10,15]. Although the ALD of metal oxides on LIB electrodes are widely studied, few reports are available on metal oxide coatings by ALD for sodium-containing intercalation electrodes [12,16]. Recently, Karthikeyan et al. demonstrated the enhancement of electrochemical behaviour of P2-\(\text{Na}_{0.66}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2\) (NMNC) at high cut-off voltage by ALD surface modification of \(\alpha\text{Al}_2\text{O}_3\) with different thicknesses for sodium ion batteries (SIB) [16].

The ALD of metal oxides on carbon substrates (nanotubes or graphene composites) has also been applied as composite electrodes for supercapacitor applications [17–22]. The enhanced capacitance of these composite electrodes could be attributed to the presence of carbon along with the metal oxide particles. Recent studies demonstrate that research on fabricating high-performance supercapacitor (EDLC) using ALD is being made toward developing high-performance composite materials [11,18,20]. It is also possible to employ ALD to stabilize the surface of the cathode in high energy Li/Na ion capacitors. It is
well-known that Li/Na ion capacitors (LIC or NIC) can deliver high energy density (ED) and power density (PD) values through the hybridization of battery and capacitor electrodes in a single device. Generally, an LIC or NIC is a single device consisting of an insertion-type cathode (battery component) and an EDLC component (super capacitor element) as a counter electrode in either aqueous or non-aqueous medium [23–25]. Despite having been explored extensively, the research activities of LIC are in an advanced stage and attempts are in progress to create conversion and alloy anodes. On the other hand, an LIC containing an insertion-type electrode in organic electrolyte showed high capacitance and ED but exhibited poor capacitance retention over long cycling which hinders its practical application [25]. To enhance the capacitance behaviour of LICs, many strategies have been established such as creating carbon or polymer composites [23,25–27].

Moreover, the scarcity of lithium resources in the earth’s crust and the complexity of lithium recycling processes are motivating the exploration of alternative electrochemical capacitors which could deliver high EDs and PDS equivalent to those of LICs. Due to availability and environmental friendliness, SIBs are anticipated to replace expensive and toxic LIBs in the near future [28]. Similar advantages are gained by replacing LICs with NICs [24,28]. Unfortunately, few sodium insertion electrodes are reported for NIC applications while numerous insertion type electrodes are available for LICs [24,29–33] Most of these NICs exhibited intense capacitance fading even in the aqueous electrolyte which is unsuitable for high ED applications [30,33–38,39]. It is vital to develop high performance NICs that can deliver enhanced electrochemical performance such as high ED and PD with our sacrificing its prolonged cycle life. The construction of NIC in an organic electrolyte is the effective way to increase the cell voltage of NIC and consequently the energy density. Recently, the fabrication of NIC with Na0.33V2O5 (NVP)/carbon as the cathode in an organic electrolyte was reported with high voltage along with 64.5% cyclic stability after 10,000 cycles [40]. In our previous work, we succeeded in fabricating an organic NIC containing carbon-coated C-NVP cathode with an excellent cyclic stability of 92% after 10,000 cycles [32]. However, NICs assembled with NASICON-NVP have low capacitance and ED values, limiting their large-scale applications [32,40,41]. Choosing cathode materials with high theoretical capacity is key to enhancing NIC capacitance behaviour. Among the intercalation cathodes reported for SIBs, P2-type layered materials possess high discharge capacity and rate performance [28]. Nevertheless, P2-type materials have poor cyclic stability due to the P2-02 phase changes at high cut-off voltages [42]. Recently, the elimination of phase changes in P2-type cathode materials using metal oxide coatings by conventional solution-based methods and ALD has been reported to enhance the Na-ion storage capability of layered materials at high voltage range [16,43,44]. Additionally, the ultrathin Al2O3 layer coated by ALD on the electrode surface displayed superior stability and rate performance due to the coating’s uniformity and conformity [16,45] Although many works propose overcoming severe capacity fading of layered materials at high voltage by introducing foreign metal elements in NIBs, their potential application in NICs are still not explored well due to the poor cycling retention during the prolonged cycles [24,28,45]. Lately, adoption of layered cathode in aqueous NIC has been reported with limited capacitive performances [33–38]. Like LICs, NICs also suffer from poor cycling performance in an organic electrolyte when tested at > 2.5 V [40]. Hence, the improvement of capacitive performance of P2 electrode active materials at high operating window is crucial to maximize the ED output and cyclability of NICs at high PD.

Herein, we present a pioneering work using ALD to fabricate superior NIC constructed with P2-layered cathode operating between 0 and 3 V in an organic electrolyte. To the best of our knowledge, this is the first report that exists on utilizing ultrathin (~ 1 nm) metal oxide coatings by ALD on a cathode surface to stabilize the EEI and construct extremely stable LICs or NICs. The NIC fabricated with Al2O3-coated NMNC (NMNC-AI) along with commercial activated carbon (CAC) displays nearly negligible capacity fading after 10,000 cycles at 0.35 A g−1 within a range of 0–3 V in 1 M NaClO4 electrolyte compared to the NIC with pristine NMNC (78% capacity fade). High-potential operation is required for large-scale storage applications as it increases the ED of the NIC, and hence we have chosen 3 V as the upper cut-off voltage for the present study. The obtained results reveal that ultrathin Al2O3 films on an NMNC cathode tailored its surface to form a stable EEI layer and dramatically enhance the electrochemical stability of pristine NMNC cathodes in a NIC cell. In addition, the implementation ALD in LICs/NICs will overcome many limitations for developing high ED and PD materials with enhanced stability at high voltage since the capacity retention normally decreases with the upper voltage limit.

2. Experimental

2.1. Preparation of NMNC

Citic acid assisted sol-gel method was used to synthesize NMNC particles where citric acid acted as a chelating agent to eliminate particle agglomeration during high-temperature calcination. In a typical synthesis, stoichiometric amounts of Na, Mn, Ni and Co acetates were dissolved in distilled water and mixed well with an aqueous solution of citric acid and then evaporated at 90 °C to obtain the gel precursors. The molar ratio of metal acetates to citric acid was fixed at 1 M. The resulting precursors were pre-calcined at 400 °C for 4 h to remove the organic acetate molecules. Finally, the obtained powders were ground and calcined at 850 °C for 12 h in air to yield the final NMNC powders.

2.2. Preparation of the NMNC electrode

The pristine NMNC electrode for ALD was prepared by a pressing a cathode slurry on stainless steel mesh. The electrode slurry contained 75 wt% of NMNC powders, 15 wt% ketjen black as a conductive additive, and 10 wt% of Teflonized acetylene black binder. The obtained electrode was dried under vacuum at 90 °C overnight before ALD coating of Al2O3. The same procedure was followed to prepare a CAC (1500 m2 g−1) anode.

2.3. ALD coating of Al2O3 thin films on the NMNC electrode

An ultrathin film of Al2O3 was directly deposited on NMNC electrode at 115 °C in an ALD system (Thermal Gemstar 6XT, Arradiance, LLC, USA). Trimethylaluminum (TMA) and H2O were used as the precursor and oxidizer, respectively, for Al2O3 coating. The purging time for TMA and water was set to 21 ms and 10 ALD cycles were performed on NMNC electrodes for NIC fabrication while 84 cycles of ALD were used on NMNC powder for physical characterization.

2.4. Physical and electrochemical characterization

As seen from Fig. 1a, one ALD cycle involves the combination of two half-cycle reactions. The Precursor molecule is supplied into the deposition chamber during the first half-cycle of the ALD process (Step 1 in Fig. 1a). In Step 1, the TAM molecule gets adsorbed on the NMNC surface forming a covalent bond with the surface molecules. After the substrate is saturated with TMA molecules, Step 2 is conducted in which the ALD chamber is purged to remove reaction by-product and the unreacted TMA. In the second half-cycle, the water is supplied into the process as the oxidation agent. During Step 3, the water is reacted with TMA and form a thin layer of Al2O3 on the surface of NMNC. Finally, the chamber is again purged to completely remove excess water and by-products (Step 4, Fig. 1a) from the chamber. This ends the first cycle of the ALD process. The half-reactions are repeated to increase the coating thickness.

Phase purity of the pristine NMNC and ALD-coated NMNC powders
were examined using X-ray powder diffraction (XRDMiniﬂex 600, Rigaku, Japan) with Kα radiation (λ = 1.5406 nm). The morphology and structure of Al2O3 coatings were observed by field emission scanning electron microscopy (FE-SEM, LEO Zeiss 1550, Switzerland), and high-resolution transmission electron microscopy (HR-TEM, JEOL 2010 FEG). The electrochemical behaviour of SIBs and NICs have performed in CR2032 coin-type cells. To fabricate SIBs, the coin cells were assembled in a glove box under an argon atmosphere by sandwiching a working electrode (CAC, NMNC, or NMNC-Al) and a pure sodium foil counter electrode separated by polypropylene separator (Celgard 2400). 1 M NaClO4 dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1; v/v) was used as the electrolyte. The same fabrication method was followed to construct a NIC where CAC acted as the anode. The charge-discharge studies (C-DC) of SIBs containing pristine or ALD-coated NMNC and CAC were carried out within a potential range of 2–4.5 V and 3–4.6 V respectively while the C-DC performance of NICs was examined between 0 and 3 V at different current densities. The C-DC studies were carried out in Land Battery Test System at ambient temperature. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical analyzer (Bio-Logic, France).

3. Results and discussion

The schematic of ALD process of Al2O3 on the NMNC is presented in Fig. 1a. The XRD patterns of pristine and Al2O3-coated NMNC are presented in Fig. 1b, which can be indexed based on a P2-type hexagonal structure with P63/mmc space group [16,43]. Both patterns do not exhibit any impurity peaks within the recorded range, conﬁrming the formation of phase-pure NMNC powders [16,28,43]. The lattice parameters for pristine and ALD samples were calculated from the XRD pattern in Fig. 1b and the a and c values are unchanged. This conﬁrms that the deposition of Al2O3 by ALD at 115 °C does not affect its structural behaviour [16]. The SEM images of pristine NMNC in Fig. S1a displays well-deﬁned particles with smooth surfaces and edges. An average particle size of 1.5 µm is observed with uniform particles size and distribution. Cathode materials with uniform size distribution are favourable for shortening the ionic migration path, resulting in better ion insertion into the host material during the C-DC process [16,27,46]. The surface of NMNC becomes rough after ALD as conﬁrmed in Fig. S1d and S1c. The presence of Al on the surface of NMNC powder is conﬁrmed by energy-dispersive X-ray spectroscopy (EDX) as shown in Fig. S2.

The presence of a coating layer on NMNC is further conﬁrmed using high-resolution TEM and the corresponding image is presented in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. The high-resolution TEM images of Al2O3-coated NMNC powders after 84 cycles of ALD are shown in Fig. 1c. 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The TEM image of NMNC-Al after 84 ALD cycles shows a uniform Al2O3 layer 9.4 nm thick on the surface of the host material. Based on this observation, it can be concluded that an ultrathin (~1 nm thickness) Al2O3 layer is present on the NMNC-Al electrode surface when 10 ALD cycles are used. This uniform metal oxide layer is crucial for enhancing high rate performance as it prevents active species dissolution into the electrolyte [16,43,45]. In addition, the Al2O3 coating provides structural stability against mechanical stresses occurring during cycling, which is beneficial for high rate performance [16,42,43,45]. The presence of Al2O3 coating layers is further confirmed through X-ray photoelectron spectroscopy (XPS) analysis and the corresponding spectra is given in Fig. 1d. The NMNC-Al sample displays the Al 2p characteristic peak at 74.4 eV whereas the pristine NMNC powder does not exhibit Al peak at the respective position, revealing the existence of alumina coating layer on NMNC surface [45].

The half-cell performance of pristine and Al2O3-coated NMNC cathodes against a sodium metal anode is examined in 1 M NaClO4 solution into the electrolyte [16,43,45]. In addition, the ultrathin coating layer acts as armour to protect the ion-conductive EEI layer, thereby preventing the consumption of active materials into the electrolyte and thus enhancing the electrochemical performance [12,15,16,28,43].

Fig. 1c. The TEM image of NMNC-Al after 84 ALD cycles shows a uniform Al2O3 layer 9.4 nm thick on the surface of the host material. Based on this observation, it can be concluded that an ultrathin (~1 nm thickness) Al2O3 layer is present on the NMNC-Al electrode surface when 10 ALD cycles are used. This uniform metal oxide layer is crucial for enhancing high rate performance as it prevents active species dissolution into the electrolyte [16,43,45]. In addition, the Al2O3 coating provides structural stability against mechanical stresses occurring during cycling, which is beneficial for high rate performance [16,42,43,45]. The presence of Al2O3 coating layers is further confirmed through X-ray photoelectron spectroscopy (XPS) analysis and the corresponding spectra is given in Fig. 1d. The NMNC-Al sample displays the Al 2p characteristic peak at 74.4 eV whereas the pristine NMNC powder does not exhibit Al peak at the respective position, revealing the existence of alumina coating layer on NMNC surface [45].

The half-cell performance of pristine and Al2O3-coated NMNC cathodes against a sodium metal anode is examined in 1 M NaClO4 within the potential range of 2–4.5 V. Fig. 2a displays the cyclic voltamogram traces of pristine and Al2O3-coated NMNC electrodes at a scan rate of 0.1 mV s⁻¹. Both CV curves show three redox peaks located at 4.25, 3.6, and 2.3 V and can be assigned to Ni⁴⁺/³⁺, Co³⁺/²⁺, Mn⁴⁺/³⁺ and redox couples respectively [16,43]. It is also evident from CV curves that the pristine electrode possesses a peak shift toward lower voltages in both positive and negative scans, indicating that the lower electrochemical polarization of pristine electrode leads to unstable Na storage behaviour [16,42,43,45]. The C-DC curves of NMNC and NMNC-Al electrodes recorded between 2 and 4.5 V are presented in Fig. 2b. Both cells exhibit three oxidation plateaus during the charging process and discharge curves also have a clear downwards slope along with three reduction steps. The position of redox plateaus in C-DC curves demonstrates that the NMNC has a complex storage mechanism, agreeing well with the CV results and reports available elsewhere [16,42,43]. The NMNC and NMNC-Al electrodes deliver a discharge capacity of 121 and 125 mAh g⁻¹ at 160 mA g⁻¹ within 2–4.5 V, which are the best values reported among other P2-type materials [16,28]. Moreover, the NMNC-Al electrode shows better initial coulombic efficiency (82%) than that of pristine NMNC (70%). The impact of the metal oxide coating on the electrochemical stability of the NMNC cathode is presented in Fig. 2c. The NMNC-Al electrode has excellent cyclic behaviour even after 175 cycles at 160 mA h g⁻¹ within 2–4.5 V. The cell with the pristine NMNC electrode delivers 35 mAh g⁻¹ discharge capacity after 175 cycles while the NMNC-Al electrode maintains more than twice this value of after 175 cycles. It is clearly demonstrated that ultrathin ALD coating of Al2O3 displays enhanced electrochemical stability during the C-DC process due to its ability to suppress the P2-O2 phase transformation at high voltage cycling processes [16,43,45]. In addition, the ultrathin coating layer acts as armour to protect the ion-conductive EEI layer, thereby preventing the consumption of active materials into the electrolyte and thus enhancing the electrode’s electrochemical performance [12,15,16,28,43].

The C-DC performance of CAC in a SIB configuration is also tested between 3 and 4.6 V at 200 mA g⁻¹ current density and the C-DC curve is presented in Fig. 2d. The CAC half-cell exhibits a non-Faradaic storage mechanism along with the adsorption/desorption of ClO₄⁻ anions on the surface which leads to the formation of a double layer at the EEL. The CAC electrode delivered a discharge capacity of 52 mAh g⁻¹ and maintained an excellent cyclic stability of 95% after 250 cycles, confirming that CAC could be used as an electroactive material for stable
NICs. In a NIC configuration, the applied voltage will split based on the capacitive performance of the individual electrode when the NIC is constructed with electrodes involving different energy storage mechanisms. Hence, it is crucial to optimize the mass balance of each electrode to fabricate high-energy NICs [48,49]. Based on the electrochemical performance obtained from NMNC, NMNC-Al, and CAC electrodes at same current density against a sodium metal anode, the optimized mass ratio of cathode to the anode to construct NICs (NMNC/CAC) is 2:1. It is known that the NMNC, NMNC-Al, and CAC electrodes become polarized during the C-DC process and act as electrodes in NIC configuration [32,49]. Thus, the electrochemical capacitive performance of NMNC/CAC and NMNC-Al/CAC NICs are tested between 0 and 3 V at different current densities.

The impact of ALD coating on the capacitive performance of NICs is initially tested using EIS analysis at the open circuit voltage between 200 kHz and 100 mHz and their Nyquist plots are presented in Fig. 3a. Good fitting data are obtained for the NIC cells based on the equivalent circuit as shown in the inset of Fig. 3a. Nyquist plots of SIBs in Fig. 3a display a semi-circle at high-frequency region and an inclined line at high-frequency region. The semi-circle at higher frequency corresponds to the charge transfer resistance ($R_{ct}$). The $R_{ct}$ represents the sum of the resistance associated with the ionic migration through the bulk of the electrode, the EEI resistance, and the electrode resistance. An inclined line observed in the low-frequency region relates to the Warburg impedance ($Z_w$) which is attributed to the diffusion-controlled process of the electrode material. It is evident from Fig. 3a that the NMNC-Al/CAC NIC has a much lower $R_{ct}$ value than the NIC containing the pristine NMNC electrode, due to the influence of surface modification by Al$_2$O$_3$ deposition. In our previous work, we have demonstrated that the ALD of Al$_2$O$_3$ can significantly reduce interfacial resistance (IR), which directly affects the cyclic stability of the energy storage system [16,50]. An increase in IR is an indication of an increase in $R_{ct}$ that affects the long-term cyclability of the cell [8,12,32]. In addition, the development of an ultrathin uniform layer of Al$_2$O$_3$ by ALD is beneficial to protect the electrode surface from the acidic electrolyte, which assist to form stable EEI layer and enhances the ionic diffusion rate even at high current densities [3,12,16,21]. Hence, an improved capacitive performance can be expected from an NMNC-CAC cell due to its low resistance value.

Fig. 3b depicts CV curves of NICs recorded within a potential range of 0–3 V at a 5 mV s$^{-1}$ scan rate in 1 M NaClO$_4$ electrolyte. The shapes of the CV traces imply that the capacitive behaviour of NICs is distinct from that of the electric double-layer capacitor (EDLC), which originates from the overlapping effect of two different energy storage mechanisms: battery and EDLC [51–53]. The CV curves also reveal that the current response between the anodic and cathodic sweep remains constant and the high symmetry indicates an excellent reversibility of the NIC cells. This appealing kinetic reactivity makes P2-NMNC and CAC electrodes a promising energy source for high-performance NIC applications. Moreover, the NMNC-Al/CAC NIC exhibits enhanced current response compared to the NMNC/CAC cell, confirming the superior energy storage property of NIC fabricated with Al$_2$O$_3$-coated NMNC. The poor capacitive behaviour of NMNC/CAC cell is attributed to the lower electronic transport as well as the sluggish reaction kinetics on the surface of the electrode [48,54,55]. In contrast, the enhanced current response of the NMNC-Al electrode is a result of the suppression of the polarization of the electrode materials during the C-DC studies [3,16,20].

The galvanostatic C-DC performances of different NICs recorded
between 0 and 3 V at 0.35 A g\(^{-1}\) current density is presented in Fig. 3c. The slight distortion in the C-DC profile shape further confirms that the NIC has a combined storage mechanism of redox and EDLC [24,25,56]. The energy storage mechanism at the CAC anode in NIC is associated to the formation of an electrical double layer through a non-Faradaic reaction together with the ClO\(_4\) anion presented in the electrolyte, whereas the NMNC cathode takes advantage from the Faradaic reaction of reversible Na\(^+\) intercalation/deintercalation, producing Pseudocapacitance behaviour, above, the possible reaction mechanism the fabricated NICs could be written as follows:

**Cathode:** Na\(_{x0.66-x}\)(Mn\(_{0.54}\)Ni\(_{0.2}\)Co\(_{0.13}\))O\(_2\)
\[ \Leftrightarrow \text{Na}_{0.66-x}(\text{Mn}_{0.54}^{+++}\text{Ni}_{0.2}^{+++}\text{Co}_{0.13}^{+++})\text{O}_2 + x\text{Na}^+ + xe^- \]

**Anode:** AC + xe \(-\rightarrow\) AC(xe\(-\rightarrow\)) + / ClO\(_4\)\(_-\)\(^{-}\) \((/\text{stands for double layer})\)

During the charging process, Na\(^+\) ions are extracted from the NNMC structure into the electrolyte and then reinserted into the NNMC electrode from the electrolyte solution during the discharge process, which confirms the high energy density of the NIC. On the other hand, ClO\(_4\) anions also get adsorbed and desorbed on the surface of the CAC electrode to produce the double layer during the C-DC process, providing the essential power density. The NMNC-Al/CAC NIC displays a higher discharge time compared to the NIC with pristine NMNC as the electrode, demonstrating that the Al\(_2\)O\(_3\) coating by ALD plays a key role in the equation enhancing the capacitive behaviour of the pristine NMNC electrode. The cell capacitance (C\(_{\text{cell}}\)) and specific capacitance (C\(_{\text{spec}}\)) is calculated using the formulae C\(_{\text{cell}}\) = \((i\Delta V)/V\) and C\(_{\text{spec}}\) = \((4 \times C_{\text{cell}})/M\) respectively, where \(i\) is the applied current density (A), \(t\) is the discharge time (s), \(\Delta V\) is the potential difference (V), and \(M\) is the total mass of the electroactive materials in two electrodes [24,25,49,57-59].

A specific capacitance of 66 and 59 F g\(^{-1}\) was obtained from the NMNC-Al/CAC and NMNC/CAC cells respectively at 0.35 A g\(^{-1}\) within a 0–3 V potential range. The enhanced electrochemical behaviour of the NIC fabricated with the metal oxide-coated electrode is derived from its low internal resistance as shown in Fig. 3c. For instance, the R\(_{\text{ct}}\) values of 26 and 66 \(\Omega\) can be calculated from the C-DC curves for NMNC-Al/CAC and NMNC/CAC cells respectively at a 0.35 A g\(^{-1}\) current density. It is well-known that the electrochemical performance of an electrode is directly related to the resistance of the cell since a higher resistance hinders the current flow on the electrode surface. Therefore, higher resistance lowers the current flow and inhibits the electroactive materials from participating in the capacitive reaction, thereby reducing the capacitance at high current rates [24,25]. Thus, a poorer capacitance performance is observed from NMNC/CAC NIC cell.

The cyclic stability of NICs tested between 0 and 3 V at 0.35 A g\(^{-1}\) current density for 5000 C-DC cycles is presented in Fig. 3d. As is evident from this figure, the ALD of Al\(_2\)O\(_3\) on an NMNC electrode has tremendously enhanced the electrode stability in a NIC. The NMNC-Al/CAC cell delivered 66 F g\(^{-1}\) and maintained a superior electrochemical reversibility of 98% even after 5000 C-DC cycles at 0.35 A g\(^{-1}\). In contrast, the NIC with the pristine NMNC electrode had 78% capacitance retention after 5000 cycles with the same cycling conditions. The outstanding stability of the NIC with the NMNC-Al electrode is ascribed to the improved structural integrity provided by ALD deposition of Al\(_2\)O\(_3\) on NMNC electrode. The presence of an ultrathin Al\(_2\)O\(_3\) layer effectively protects the NNMC surface from electrolyte attack and reduces the electrode dissolution into the electrolyte, maintaining a stable EEI and results in improved discharge capacitance and cyclability of NMNC-Al/CAC cell [3,20,21]. Moreover, the higher electrical band-gap energy of 9 eV from the ALD of Al\(_2\)O\(_3\) minimizes the structural transformation of the NMNC electrode, enhancing the electrochemical stability of the NMNC-Al/CAC cell compared to the NMNC/CAC NIC [16]. As described earlier, the ALD of Al\(_2\)O\(_3\) not only assists in protecting the cathode from the harmful electrolyte during the C-DC process but also decreases the electrochemical impedance of NIC cells.

In order to investigate the causes for achieving improved stability in NICs containing ALD-modified electrodes, EIS measurements were conducted for the NIC cells after cycling at 0.35 A g\(^{-1}\) for 5000 cycles. Fig. 4a and Fig. S3 compare the Nyquist plots of NMNC/CAC and NMNC-Al/CAC cells recorded before and after different cycles. The Nyquist plot of the NMNC/CAC cell shows distinct changes in R\(_{\text{ct}}\) values after cycling whereas the NIC containing the ALD-modified NMNC electrode displays identical curves at all C-DC cycles. As proven from Fig. 4a, the ALD of Al\(_2\)O\(_3\) played an important role in shielding the EEI from dissolution, which suppressed the electrode polarization [1,16]. The comparison of R\(_{\text{ct}}\) of different NIC cells against the cycle number is presented in Fig. 4b, which reveals that the increase in R\(_{\text{ct}}\) values upon cycling is much higher for the NMNC/CAC cell. The values of R\(_{\text{ct}}\) for the NMNC/CAC cell are about 26, 56 and 137 \(\Omega\) at the initial, 2000th and 5000th cycles respectively. In contrast, the R\(_{\text{ct}}\) of NMNC-Al/CAC cell in the initial cycle is 19 \(\Omega\) and remains constant even after 5000 cycles, indicating better surface protection, which is essential for obtaining superior electrochemical stability even at high rates [1,5,12,16]. Based
on the discussion above, an ultrathin Al₂O₃ layer generated by ALD provides greater assistance for diminishing electroactive species dissolution into the electrolyte while maintaining the structural integrity of the NMNC cathode material upon extended C-DC cycling processes.

The rate performance of NICs at varying current rates are given in Fig. 5a. As expected, the discharge capacitance of NICs decreases with increased current density due to the diffusion control process as only the outer surface of the electrode material participates in the C-DC process at high current rates [23,25]. The NMNC-Al/CAC cell has improved discharge capacitance compared to the NMNC/CAC cell at all current densities as presented in Fig. 5a. Impressively, the NIC constructed with the ALD-coated electrode delivered 56 F g⁻¹ at 1.1 A g⁻¹ current density, which is more than 70% of the capacitance delivered at the lower current density. In contrast, the NMNC/CAC cell had a capacitance of only 32 F g⁻¹ at 1.1 A g⁻¹ current density, which is more than 70% of the capacitance delivered at the lower current density. The coating layer can provide a flexible barrier against the EEI layer against erosion by rapid electrolyte attack at high current densities [5,16]. Additionally, this EEI dissolution of the active species in acidic electrolyte reduces the active surface for storage reaction and thus capacitance is decreased at high currents for NIC with a non-modified electrode.

The long-term cyclability is critical for any energy storage device to be employed in practical application. Thus, the prolonged stability of the NMNC-Al/CAC cell is tested at various current densities and the results are presented in Fig. 5b. A total of 5000 C-DC cycles at 0.45, 0.55 A g⁻¹ and 10,000 C-DC cycles at 0.35 and 0.72 A g⁻¹ are tested at ambient temperature. The NMNC-Al/CAC cell delivered a capacitance of 72, 58, 57, and 56 F g⁻¹ at current densities of 0.35, 0.45, 0.55, and 0.72 A g⁻¹ respectively and maintained 98% of its initial values upon extended C-DC cycling. It is noteworthy that this is the first report on a NIC constructed with a sodium intercalated layered cathode with prolonged cyclic life performance at high current densities in an organic electrolyte. Most of the work of NICs containing layered materials are demonstrated in an aqueous electrolyte with severe capacity fading. For instance, Na₀.₆₇Al₀.₃Co₀.₇O₂ nanopowders are reported to exhibit 80% capacity retention after 5000 C-DC cycles between 0 and 1 V [37]. Recently, Na₃V₂(PO₄)₃/AC NIC system has been reported with over 90% capacitance retention after 10,000 cycles. However, this NIC exhibited poor rate performance and PD values, which is not suitable for practical applications [32]. Fig. 5c compares the stability of NMNC-Al/CAC with various NIC systems reported elsewhere, confirming the outstanding stability of the NIC with an ALD-modified NMNC electrode [10,24,29,30,32–35,60–62]. This superior cycling stability of a NIC containing an NMNC-Al cathode is ascribed to the structural integrity provided by the ALD of Al₂O₃. This ultrathin metal oxide layer of the NMNC-Al electrode can accommodate the volume change due to the inherent mechanical stress and strain during the cycling process [16,45]. The coating layer can provide a flexible barrier against the stress and strain within the electrode during the cycling process, which
leads to better electrochemical behaviour \[3,15,16,20\]. The low $R_{dd}$ of the NMNC-Al/CAC cell at all current densities also aids its excellent electrochemical stability. The plot of RIR versus current densities for the NMNC-Al/CAC cell within 0–3 V is shown in Fig. 5d. The NIC with the NMNC-Al cathode maintained lower internal resistance values at all current densities, demonstrating the higher current flow on the surface of NMNC-Al. This high current flow ensures more Na ion diffusion toward the electrode surface, enhancing the cycling behaviour remarkably even at high current rates \[24,25,47,56\].

Fig. 6a illustrates the Ragone’s plot of NICs as a function of ED and PDs measured from C–DC studies at different current densities. The power and energy density values are calculated based on the formula reported elsewhere \[63\]. This figure shows that the NMNC-Al/CAC cell has much higher ED characteristics compared to the NMNC/CAC cell. In the case of the NIC with NMNC-Al, an ED of 82 Wh kg$^{-1}$ is attained at a PD of 1350 W kg$^{-1}$, whereas the NMNC/CAC cell has ED of about 70 Wh kg$^{-1}$ at the same PD value. The NMNC-Al/CAC cell still maintained 63 Wh kg$^{-1}$ even at a high PD of 6.6 kW kg$^{-1}$. In contrast, the NMNC/CAC cell provided a 36 Wh kg$^{-1}$ ED at a PD of 6.6 kW kg$^{-1}$. Moreover, the ED obtained at a very high PD value is the best ever reported among NICs constructed with sodium-based intercalation electrode materials and also exceed many lithium ion capacitors \[19,24,25,30,32,36,46–48,54,56\]. This excellent electrochemical performance of NMNC-Al/CAC is a result of protecting the EEI layer by the ALD modification of the NMNC surface \[3,12,16\]. This is confirmed by recording the EIS spectrum before and after 2000, 5000, 10,000, and 20,000 cycles at different current rates which are presented in Fig. 6b. The diameter of the semi-circle at a medium frequency range remains unchanged even after 20,000 cycles, confirming its superior electrochemical stability. The comparison of $R_{ct}$ against the number of cycles is shown in Fig. 6c. The $R_{ct}$ value of the NMNC-Al/CAC cell before cycling is 18.3 $\Omega$ and the cell still has very low $R_{ct}$ of 24.1 $\Omega$ even after 20,000 cycles, which confirms that the EEI layer is effectively protected by the ultrathin Al$_2$O$_3$ layer. Thus, exceptional energy storage performance is achieved with the NMNC-Al electrode. In addition, the NIC with the NMNC-Al cathode exhibits a low IR drop even at a high current density of 2.2 A g$^{-1}$ as presented in Fig. 6d.

Based on above outcomes, the schematic diagram of the protecting role of ALD Al$_2$O$_3$ layer is presented in Fig. 7. It has been confirmed that the ultra-thin uniform ALD coating of Al$_2$O$_3$ layer as an artificial EEI and forms a stable interface between NMNC electrode and electrolyte. This effectively suppressing the occurrence of side-reactions with electrolyte species (ClO$_4^-$) and dissolution of electrode active species. Our work demonstrates that ALD could be considered as an effective performance enhancement technique for any advanced hybrid capacitor for high energy applications with high specific energy and power without decreasing their cycling performance.

### 4. Conclusion

For the first time, ALD has been implemented to improve the electrochemical behaviour of a NIC by the deposition of a uniform ultrathin Al$_2$O$_3$ coating on the NMNC electrode surface with. Our study demonstrates that a NIC fabricated with a CAC anode and an NMNC cathode modified by ALD delivers a discharge capacity, energy density, and power density of 66 F g$^{-1}$, 75 Wh kg$^{-1}$, and 2.23 kW kg$^{-1}$.
respectively at 0.35 A g\(^{-1}\) along with an extremely stable cyclic stability of 98% after 10,000 cycles. The NIC with a pristine NMNC cathode shows inferior electrochemical performance and stability at all current densities. The improved rate capability can be attributed to the lower impedance and lower ohmic drop arising from the surface protection by ALD. This dramatic performance improvement may also be a result of the ultrathin Al\(_2\)O\(_3\) ALD film acting to minimize active species dissolution, maintain the structural integrity of the NMNC and protect the cathode surface from electrolyte side reactions. Consequently, this work not only demonstrated that ALD can be used to coat a uniform metal oxide layer on a NIC cathode but also proved that it has a noteworthy effect on the electrochemical performance of NICS.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2018.03.021.

References


Fig. 7. Schematic diagrams of the shielding effect of ultra-thin ALD Al\(_2\)O\(_3\) layer on the NMNC electrode.
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