

Article

# Production of Large Specific Capacitance by Electrodes with Low Active Mass and Synergistic Mechanisms

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**ABSTRACT:** Decoration of vanadium nitride nanoparticles on carbon nanotubes creates electrodes with three different energy storage mechanisms that operate synergistically to give a high specific capacitance with a low active mass. Calculation and measurements further indicate the power and energy density to be as high as  $10^5-10^6$  W/kg and  $10^2$  Wh/kg, respectively. Particle attachment also greatly improves the capacitive coefficient, including ionic transmittance, charge transfer, porosity, and conductivity. Corrosion tests based on the Tafel method reveal the corrosion potential and current of electrodes as low as -0.721 V and  $7.53 \times 10^{-4}$  A, respectively.

## 1. INTRODUCTION

Energy storage plays an important part in renewable energy systems and various devices have been developed such as thermochemical conversion,<sup>1-3</sup> mechanically driven type,<sup>4,5</sup> and electrochemical energy storage. Among others, energy storage through electrochemical mean prevails mainly due to its capability of producing high specific capacitance  $(C_s)$  and wide potential range.<sup>6</sup> Owing to their fast rate performance and high power density, the electrochemical capacitors (supercapacitors) have become the subject of great interest in the electrochemical society.<sup>7,8</sup> The study indicates two mechanisms involved in ionic absorption-desorption at electrode surfaces where the faradaic redox reaction (FROR) yields greater  $C_{\rm s}$  than does the electric double-layer charging (EDLC).<sup>9–13</sup> Accordingly, a recent study focuses on transitional compounds with high oxidation states and electrical conductivity ( $\sigma$ ), e.g., RuO<sub>2</sub>,<sup>14</sup> V<sub>6</sub>O<sub>13</sub>/VO<sub>2</sub>,<sup>15</sup> V<sub>2</sub>O<sub>5</sub>,<sup>16</sup> CuCo<sub>2</sub>O<sub>4</sub>,<sup>17</sup> Co<sub>3</sub>N,<sup>18</sup> Ni<sub>3</sub>N,<sup>19</sup> CrN,<sup>20</sup> VN, and their  $CuCo_2O_4$ , <sup>17</sup>  $Co_3N$ , <sup>18</sup>  $Ni_3N$ , <sup>19</sup> CrN, <sup>20</sup> VN, and their composites. <sup>21,27</sup> These, however, are often made in conjunction with plastic binders, thus significantly reducing the electrochemical performance. Carbon nanotubes (CNTs) are sp<sup>2</sup>-bonded one-dimensional conductors and, similar to graphite and graphene, are also governed by EDLC.<sup>28</sup> Material hybridization has been proved to be efficient in improving the electrochemical performance of CNT-based electrodes, for example, composite electrodes made from homogeneous mixing of CNTs and VN. In this case, CNTs are added to improve  $\sigma_i$  and energy storage mainly proceeds through VNcreated FROR (1, Figure 1a).<sup>29</sup> Ion-intercalation mechanism (ITC), on the other hand, emerges as electrodes consist of core-shell nanostructures (i.e., VN-coated CNTs, 1 and 2, Figure 1b).<sup>30</sup> Unlike conventional techniques that make electrochemical electrodes with large surface area and





Figure 1. Three types of electrochemical electrodes. Electrode with FROR (1) arising from VN (a). Electrode with FROR (1) from VN and ITC (2) from the grooves between VN-coated CNTs (b). Electrode with FROR (1) from VN particles, ITC (2) from grooves between CNTs, and EDLC (3) from CNT surfaces (c).

thickness,<sup>31,32</sup> this work, in contrast, tends to produce a large  $C_s$  on a low active mass as per the following; (i) an electrode made of thick active mass is indeed unnecessary since charge–discharge (i.e., redox reaction) takes place mainly at the surfaces;<sup>33</sup> (ii) a low active mass electrode means a reduced resistance, which is important in terms of power density.<sup>8,9</sup> This goal may be achieved by decorating VN nanoparticles on CNTs where three mechanisms synergistically operate to give a large amount of  $C_s$  (1, 2, and 3, Figure 1c). Measurements confirm a large  $C_s$  production and further indicate that the attached VN nanoparticles greatly promote the electrochemical

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© 2024 The Authors. Published by American Chemical Society activities of CNTs, including ionic transmittance, charge transfer, porosity, and  $\sigma$ . Comparison is also made on pure VN electrodes.

## 2. EXPERIMENTAL SECTION

Electrodes with hydrophilicity are of importance because FROR and EDLC operate on the basis of good wetting at the solid–liquid interface. Multiwalled CNTs made by metal catalytic pyrolysis of hydrocarbons (purity >90%, L-MWCNT1020, CONJUTEK, Taiwan) are treated with concentrated acid (2 M HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>, 50 °C) to improve the tube wetting and dispersion in aqueous solution.<sup>34</sup> The synthetic procedures of electrodes are summarized in Figure 2a



**Figure 2.** Fabrication of VN/CNTs/Ni electrodes (a). SEM images obtained from Ni net before CNT and VN coatings (b). CNT-coated Ni and highlighted image of CNTs (inset) (c), and the surface texture of VN/CNTs (d).

and are briefed as follows. Nickel (Ni) possesses a high resistance to corrosive solutions and is therefore used as a current collector.<sup>35</sup> A Ni net (spacing = 20 mm,  $5 \times 5$  cm, 6N, 300 mesh, twill weave) is dipped into a CNT suspension made by ultrasonically dispersing treated CNTs (100 mg) in Mg  $(NO_3)_2$ ·6H<sub>2</sub>O (17 mg) dissolved in methanol (200 mL). The Ni net is electrified to electrophoretically transfer CNTs to metal surfaces (current = 3-5 mA, voltage = 70 V, and treating time = 10 min),<sup>36</sup> and the amount of transferred CNTs is as low as 5-7 mg, as per the measurements by a microbalance. The CNT-coated Ni net is then immersed in  $V_2O_5$  (Showa, 99.5%, 3 g) dispersed in  $H_2O_2$  for xerogel coating (Sigma-Aldrich, 4.3 wt %, 250 mL, 40-80 °C).37 The oxide-coated CNT-Ni electrode is rinsed with distilled water to remove excess of oxide gel, followed by heating in anhydrous ammonia atmosphere at 600 °C for 6 h of nitridation (i.e.,  $V_2O_5 + 10/3$  $NH_3 \rightarrow 2VN + 5H_2O + 2/3N_2$ .<sup>38,39</sup> The resultant materials are hereafter defined as VN/CNTs/Nit, where the subscript t denotes the deposition time of xerogel and is set at 15 and 30 min respectively (i.e., VN/CNTs/Ni<sub>15</sub> and VN/CNTs/Ni<sub>30</sub>). CNT-free samples (i.e., VN/Nit) with a similar t and oxide content (<2%) are also made and tested for comparison. Capacitive coefficients are characterized by cyclic voltammetry (CV) as follows. VN/CNTs/Nit are used as working electrodes in conjunction with Pt-counter and Ag/AgClreference electrodes to measure redox potentials in two types of neutral electrolytes for comparison, i.e., 4 M LiCl<sub>(aq)</sub> and 1.6 M LiCl<sub>(aq)</sub> dissolved in  $C_2H_5OH$  defined as el-A and -B. It is worth mentioning that LiCl<sub>(aq)</sub> is a neutral solution with the standard electrode potential  $\rm ({\check E}^o/V)$  as high as  $-3.04~\rm (Li$   $\rightarrow$  $Li^+ + e^-$ ) and is therefore used as an electrolyte.<sup>33</sup> Since electrolysis of water occurs as the charging potential exceeds 1

V, the scan window  $(S_w)$  and rate  $(S_r)$  are set at -1 to -0.25 V and  $10-50 \text{ mV s}^{-1}$  for el-A. el-B, on the other hand, has a lower  $\sigma$  and is therefore tested in a wider  $S_w$  (-1.75–0 V). Electrochemical impedance spectra (ECIS) of the working electrodes are recorded at 10 mHz-100 kHz (5 mV), and the obtained Nyquist plots (i.e.,  $Z_{re}-Z_{im}$  profiles) are analyzed with View software to uncover equivalent circuits at solidliquid interfaces, where  $Z_{\rm re}$  and  $Z_{\rm im}$  denote the real and imaginary parts of the diffusive impedance. The structures and chemical composition of electrodes are inspected by X-ray diffraction (XRD, Shimadzu 6000, Cu/K $\alpha$  radiation source), Raman analysis (LABRAM HR 800 UV, He/Ne excitation source,  $\lambda = 632.8$  nm), field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010, 15 kV accelerating voltage), high-resolution transmission electron microscopy (HRTEM, JEOL ARM-200F) equipped with an energydispersive spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Al/K $\alpha$  radiation source); the XPS profiles have been calibrated with XPSPEAK41 software, NIST database, and C 1s peak at 284.6 eV. The specific surface area  $(S_{BET})$  is measured by the nitrogen adsorption (N<sub>A</sub>) technique at 77 K (ASTM D3663-92).

### 3. RESULTS AND DISCUSSION

SEM inspections confirm the (i) deposition of CNTs onto Ni net and (ii) conversion of  $V_2O_5$  into VN nanoparticles on CNTs (Figure 2b,c and insert, Figure 2c); the latter is further verified by enhanced SEM (Figure 2d), HRTEM images (Figure 3a-c), and EDS profiles, where C, O, V, and N are measured to be 25.9, 13.4, 38.3, and 22.4 wt % (Figure S1, Supporting Information).

Figure 3d shows the EDS mapping recorded from Figure 3c, where C, N, and V arise from CNT and VN, and O is due to residual oxides arising from coatings, as evident by different diameters, i.e., 40 nm for nitride and 50 nm for oxide (Figure 3d).

XRD data agree with those of TEM and EDS and show reflections arising from the crystallographic planes of CNT (002) ( $2\theta = 26.3^{\circ}$ ) and cubic VN (111) ( $2\theta = 37.6^{\circ}$ ), (200) ( $2\theta = 43.7^{\circ}$ ), (220) ( $2\theta = 63.7^{\circ}$ ), and (311) ( $2\theta = 76.4^{\circ}$ ) (Figure 3e),<sup>40</sup> where VN formation is also verified by XPS peaks at 396.8 and 513.8 eV, corresponding to N 1s and V<sub>2</sub>p<sup>3</sup> (Figure 3f-h).<sup>23,31</sup> Additional evidence in support of V<sub>2</sub>O<sub>5</sub>  $\rightarrow$ VN conversion comes from (i) a trace of oxides after 20 s Ar plasma cleaning, i.e., V<sup>3+</sup>(curve 1, 515 eV), V<sup>4+</sup> (curve 2, 516.3 eV), and V<sup>5+</sup> (curve 3, 517.1 eV) (Figure 3g,h);<sup>23</sup> (ii) nitridation that created pyridinic-N at tube surfaces (398.6 eV, N 1s spectra, Figure 3f);<sup>41</sup> (iii) the V–N vibrations that induced Raman  $A_g$  (96, 194, 404, 525, and 992 cm<sup>-1</sup>) and  $B_{1g}$ modes (40, 283, and 694 cm<sup>-1</sup>) (Figure 4a).

However, the CNT structure remains unchanged upon V<sub>2</sub>O<sub>5</sub>  $\rightarrow$  VN conversion, as evident by the detection of D- (1330 cm<sup>-1</sup>,  $A_{1g}$ ) and G-bands (1576 cm<sup>-1</sup>,  $E_{2g}$ ) arising from the phonon scattering at zone boundaries and C–C bond vibrations. Again, the high ratio of D- to G-band intensity ( $I_{\rm D}/I_{\rm G}$  = 0.998) and hydrogen-bonded amorphous carbon profile (peak a) verify CNTs to be made by catalytic pyrolysis (Figure 4b).<sup>42,43</sup>

The study also reveals (i)  $VN_M \propto t$  and (ii)  $VN_{M(CNTs/Ni)} > VN_{M(Ni)}$ , where  $VN_M$  denotes coating the mass of VN and is only 1/6-1/9 of the reported data.<sup>25,28-33</sup> (i) is consistent



**Figure 3.** HRTEM images of VN particles on MWCNTs (a, c) and dark-field TEM images and the corresponding elemental mappings (d). XRD of VN/CNTs/Ni electrodes (e); XPS of N 1s (f) and  $V_2p^3$  (g, h); deconvoluted curve 1 for  $V^{3+}$  (515 eV), curve 2 for  $V^{4+}$  (516.3 eV), and curve 3 for  $V^{5+}$  (517.1 eV).



**Figure 4.** Raman spectra of VN (a) and CNTs (b). The peak a comes from hydrogen-bonded amorphous carbons (H-C).

with Table 1 and a report,<sup>39</sup> and (ii) indicates VN growth through oxygenated CNTs acting as templates.<sup>36</sup>

Figure 5a,b confirms the presence of oxygenated lattices in CNTs, where the content of carbonyl, hydroxyl, and carboxylic acid groups is 12.89, 8.54, and 9.8% based on the integration of XPS-C 1s and-O 1s spectra. In O 1s spectra, signals mainly come from VN and only ca. 10% for  $V_2O_5$ .<sup>31</sup>

Table 1. Content of $C_{1s}$ ,	O <sub>1s</sub> ,	and N <sub>1s</sub>	According	to
Deconvoluted XPS Spec	tra			

sample	$VN_M (mg/cm^2)$
VN/CNTs/Ni <sub>30</sub>	$0.596 \pm 0.02$
VN/CNTs/Ni <sub>15</sub>	$0.267 \pm 0.015$
VN/Ni <sub>30</sub>	$0.337 \pm 0.051$
VN/Ni <sub>15</sub>	$0.0633 \pm 0.003$

Table 2 lists  $N_A$  and  $S_{BET}$  of VN/CNTs/Ni<sub>t</sub> and VN/Ni<sub>t</sub>. Clearly, the coating of VN nanoparticles improves the electrode porosity, and improvement even reaches 2–3 orders of magnitude for VN/CNTs/Ni<sub>15</sub>. The prolonged coating of VN nanoparticles however retards gas diffusion into micropores, so  $N_A$  and  $S_{BET}$  decrease, accounting for  $N_{A(VN/CNTs/Ni15)} > S_{BET(VN/CNTs/Ni130)}$ .

Figure 6a presents the CV profiles obtained from el-A at  $S_r = 10 \text{ mV s}^{-1}$  and  $S_w = -0.25 \text{ to } -1 \text{ V}$ . Apparently, profiles are asymmetric, and current density ( $I_D$ ) follows the sequence VN/CNTs/Ni<sub>30</sub> > VN/CNTs/Ni<sub>15</sub> > VN/Ni<sub>30</sub> > VN/Ni<sub>15</sub>, attributable to the trapping of cations in VN particles.<sup>45</sup> Note that Ni current collector has a very low  $C_s$  (dark curve, Figures 6a and S3, Supporting Information).



Figure 5. XPS of C 1s (a) and O 1s (b) after Ar plasma cleaning.

$\mathbf{T}$	Table 2. N <sub>4</sub> and	l S <sub>ret</sub> of	'VN/	'CNTs/Ni	and	l VN/	'Ni
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samples	$N_{\rm A}~({\rm cm^2/g})$	$S_{\rm BET}~({\rm cm}^2/{\rm g})$
VN/CNTs/Ni <sub>30</sub>	0.0816	0.3552
VN/CNTs/Ni <sub>15</sub>	1.893	8.243
VN/Ni <sub>30</sub>	0.0089	0.03884
VN/Ni <sub>15</sub>	immeasurable	

Experiments carried out in el-B yield a similar result where two pairs of redox peaks at -0.59 and -1.35 V on positive and -0.53 and -1.3 V on negative potential arise from different  $S_w$ and solvation shells (Figure 6b).<sup>25,26</sup> We then calculate  $C_s$  as per equation  $C_s = Q/\Delta V \cdot m$  (eq 1), where m is the mass of active materials ( $\approx VN_M$ ),  $\Delta V$  is the working potential, and Q is charge (= half-integrated area of the CV curve divided by  $S_r$ ).<sup>11</sup> Compared with the reported data, VN/CNTs/Ni15 and VN/  $CNTs/Ni_{30}$  exhibit a greater  $C_s$ ; the former reaches a value as high as 511  $\text{F}\cdot\text{g}^{-1}$  in **el-A** and 468  $\text{F}\cdot\text{g}^{-1}$  in **el-B** (Figure 6c).<sup>21-25</sup>  $C_{s(VN/CNTs/Ni15)} > C_{s(VN/CNTs/Ni30)}$  is consistent with Table 2 and again confirms that VN coating promoted  $N_{A}$ ,  $S_{\rm BET}$ , and  $C_{\rm s}$ . VN/Ni, on the other hand, has limited  $N_{\rm A}$  and  $S_{\text{BET}}$ , thus giving low  $C_{\text{s}}$ .

Figure 7a displays the  $C_s$ - $S_r$  profiles of VN/CNTs/Ni<sub>30</sub> and  $VN/CNTs/Ni_{15}$ , where data points are extracted from  $I_D - S_w$ plots (Figure S2, Supporting Information). Clearly, the profiles reveal  $C_{s(VN/CNTs/Ni15)} > C_{s(VN/CNTs/Ni30)}$  and agree with the sequence  $N_{A(VN/CNTs/Ni15)} > N_{A(VN/CNTs/Ni30)}$  and  $S_{\text{BET}(\text{VN/CNTs/Ni15})} > S_{\text{BET}(\text{VN/CNTs/Ni30})}$ , as observed in Table 2 and Figure 6c.  $C_{\text{s}} \propto S_{\text{r}}^{-1}$  is indeed expected, since charge– discharge is time-dependent, and measurements give  $C_s =$ 69.2% for VN/CNTs/Ni<sub>15</sub> and 50.5% for VN/CNTs/Ni<sub>30</sub> at  $S_r = 50 \text{ mV s}^{-1}$ . Note in the Helmholtz equation that  $C_s$  is inversely proportional to the diameter (D) of solvated ions

 $[M^+(H_2O)_n]$  at interfaces,<sup>24</sup> where ethanol hydrates with ions, thus resulting in a greater **D** [i.e.,  $M^+(CH_3CH_2OH)_n$ ] and  $C_{s}(el-A) > C_{s}(el-B)$  (Figure 7a).

Since FROR associates with chemical loss over repeated charge-discharge cycles, the retention experiments are therefore carried out in few hundreds of cycles.<sup>38,39,46</sup> Figure 7b shows  $C_s$  retention over 500 charge-discharge cycles at  $S_r = 20$ mV  $s^{-1}$ , and profiles can be divided into two regions; the first lies in 1–150 cycles, where  $C_s$  decreases rapidly (Figure 7b). Profiles then level off in the second region (>150 cycles), with retention measured to be 54.6% (el-A) and 47.9% (el-B) for  $VN/CNTs/Ni_{15}$  and 59% (el-A) and 76.9% (el-B) for VN/ $CNTs/Ni_{30}$ . The C<sub>s</sub> decrease in the first region is due to the insertion of cations into VN lattices and VN oxidation; the former forms solid solution and is irreversible.<sup>46</sup> The latter produces surface roughness and holey structures (Figure 8a,b). It is worth mentioning that VN and V<sub>2</sub>O<sub>5</sub> are nontoxic and can be recycled into metallurgy additives. 47-51

 $P_{D}$  and  $E_{D}$  are important parameters widely used to justify the electrode performance and are expressed as  $P_D = V^2/4R_s m$ (eq 2) and  $\mathbf{E}_{\mathbf{D}} = C_{s}V^{2}/2$  (eq 3), where V corresponds to  $S_{w}$ , and  $R_s$  is the equivalent series resistance of the electrode and electrolyte. Table S1 (Supporting Information) lists  $P_D$  and  $E_D$ obtained from el-A and -B defined as  $P_{D(el-A)}$ ,  $P_{D(el-B)}$ ,  $E_{D(el-A)}$ , and  $E_{D(el-B)}$ . Apparently, both exceed the reported data ( $P_D = 104 \text{ W/kg}$  and  $E_D = 10-20 \text{ Wh/kg}$ )<sup>52</sup> and follow the sequences: (i)  $P_{D(VN/Ni)} > P_{D(VN/CNTs/Ni)}$ ; (ii)  $E_{D(VN/CNTs/Ni)} >$  $\mathbf{E}_{\mathbf{D}(VN/Ni)}$ ; and (iii)  $\mathbf{E}_{\mathbf{D}(el-A)} < \mathbf{E}_{\mathbf{D}(el-B)}$ . Equation 2 and Table 1 account for (i), and (iii) is due to  $E_D \propto S_w$ .<sup>52</sup> (ii) again verifies that the VN coating improved  $N_{A}$ ,  $S_{BET}$ , and  $C_s$  (Table 2 and Figure 6). ItFulate  $P_D$  and  $E_D$  as per report.<sup>53,54</sup> Table 3 lists the recalculated  $P_D$  and  $E_D$  values which exceed the reported data.55-57



Figure 6. CV profiles of VN/Ni<sub>15</sub>, VN/Ni<sub>30</sub>, VN/CNTs/Ni<sub>15</sub>, and VN/CNTs/Ni<sub>30</sub> obtained from el-A (a) and el-B (b) at 10 mV s<sup>-1</sup>. C<sub>s</sub> charts of  $VN/CNTs/Ni_t$  and  $VN/Ni_t$  obtained from el-A and el-B (c).

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Figure 7.  $C_s$ - $S_r$  (a) and  $C_s$  retention profiles (b) of VN/CNTs/Nit and VN/Nit in el-A and el-B.



Figure 8. SEM images of used VN/CNTs/Ni15 electrodes (a) and a zoomed-in image where holey structures are circled (b).

Table 3.  $P_{\rm D}$  and  $E_{\rm D}$  of VN/CNTs/Ni\_t and VN/Ni\_t in el-A and el-B

	e	l-A	e	l-B
samples	$P_{D} \ (W/kg)$	$E_D$ (Wh/kg)	$P_D$ (W/kg)	$E_D$ (Wh/kg)
VN/CNTs/Ni <sub>15</sub>	129600.1	25.56	10953.9	78.75
VN/CNTs/Ni <sub>30</sub>	50066.1	15.94	44099	40.96
VN/Ni <sub>15</sub>	609404.2	13.13	321158	27.16
VN/Ni <sub>30</sub>	139672.1	8.17	31877.2	22.02

The ECIS values of VN/CNTs/Ni<sub>t</sub> are analyzed on the basis of equivalent circuits that contain  $R_s$ , a parallel combination of constant phase element (CPE), diffusive resistance ( $R_d$ ), charge-transfer resistance ( $R_{ct}$ ), and double-layer capacitance (CPE<sub>dl</sub>). CPE is calculated according to  $Z_{CPE} = 1/T(i\omega)^p$  (eq 4), where *T* is the CPE constant (unit: Fs<sup>(p-1)</sup> cm<sup>-2</sup>),  $\omega$  is angular frequency, *P* is phase angle, and *P* = 1 represents an ideal capacitor.<sup>57–59</sup> Note that Warburg impedance is excluded from ECIS because it arises from the electrode bulk and cannot depict the diffusion of ions into nanostructures.<sup>57</sup> Table 4 lists the related parameters, and the  $Z_{re}-Z_{im}$  plots are shown in Figure 9a,b.

First, charge-discharge in el-A exhibits a time constant (semicircle) arising from the parallel combination of CPE<sub>dl</sub> with  $R_s$ ,  $R_{ct}$ , and  $R_d$  (insets, Figure 9a). Second,  $R_{s(el-A)} < R_{s(el-B)}$ verifies a greater ionic conductivity in aqueous solution, the electrolyte conductivity being measured to be 60-65 m·S/cm for el-A and 11.6 m·S/cm for el-B. Third,  $R_{ct(el-A)} \ll R_{ct(el-B)}$ indicates a greater ionic admittance in el-A (Table 4). Charge transfer in el-B, however, requires a greater activation energy across the double layer at the interface, so CPE<sub>dl</sub>-T is low, and the  $Z_{\rm re}-Z_{\rm im}$  plot exhibits two time constants; the lowfrequency one comes from the additional CPE connected in series with  $R_{ct}$  (blue circle, Figure 9b).<sup>31,60</sup> Fourth, the VN coating promotes CPE-T by 1–2 orders of magnitude.<sup>61</sup> Fifth, CPE<sub>dl</sub>-P and CPE-P in el-A and -B are comparable. In other words, the increased  $C_s$  and  $R_{d(VN/CNTs/Ni)} > R_{d(VN/Ni)}$  truly originate from VN coating that improved porosity, ion accessibility, charge transfer, and  $\sigma$ . In addition to  $C_s$ promotion, electrodes may corrode in polar electrolytes, thus

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Table	4.	Electroc	hemical	Parameters	of	VN/	/CNTs	/Ni	and	VN	/Ni	in	el-A	and	el	-B
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el-A	R <sub>s</sub>	CPE <sub>dl</sub> -T	CPE <sub>dl</sub> -P	$R_{\rm ct}$	CPE-T	CPE-P	R <sub>d</sub>
VN/CNTs/Ni <sub>15</sub>	2.464	0.032	0.9924	3.803	0.044	0.798	516.2
VN/CNTs/Ni <sub>30</sub>	2.921	0.032	0.981	3.539	0.04	0.770	501
VN/Ni <sub>15</sub>	2.321	$2 \times 10^{-4}$	0.945	2.694	$1.5 \times 10^{-3}$	0.702	585.5
VN/Ni <sub>30</sub>	2.255	$1.1 \times 10^{-3}$	0.9715	4.234	$5 \times 10^{-3}$	0.725	513
el-B	R <sub>S</sub>	CPE <sub>dl</sub> -T	CPE <sub>dl</sub> -P	R <sub>ct</sub>	CPE-T	CPE-P	R <sub>d</sub>
VN/CNTs/Ni <sub>15</sub>	10.47	$1.34 \times 10^{-5}$	0.797	50.05	0.018	0.847	509
VN/CNTs/Ni <sub>30</sub>	11.91	$9.36 \times 10^{-6}$	0.847	48.15	0.018	0.835	555
VN/Ni <sub>15</sub>	14.88	$9.6 \times 10^{-6}$	0.818	52.82	$5.2 \times 10^{-4}$	0.664	1145
VN/Ni <sub>30</sub>	24.45	$8.73 \times 10^{-6}$	0.883	48.24	$1.45 \times 10^{-3}$	0.736	1141



Figure 9.  $Z_{re}-Z_{im}$  plots of VN/CNTs/Ni<sub>t</sub> and VN/Ni<sub>t</sub> in el-A (a) and el-B (b); insets display the corresponding equivalent circuits. Circled part denotes the formation of additional CPE in el-B, which creates the second time constant at a low frequency.

reducing  $C_s$  and retention. Corrosion tests are carried out using the Tafel method, and the corrosion potential  $(V_{cor})$  and current  $(I_{\rm cor})$  are measured at the linear region of the  $V_{\rm cor}$  $logI_{ap}$  plot, where  $I_{ap}$  is applied current.<sup>62</sup> Extrapolation at the linear region (= 50 mV) gives  $V_{\rm cor}$  = -0.721 and  $I_{\rm cor}$  = 7.53 ×  $10^{-4}$  for Ni meshes, values which are low and approximate that of CNTs ( $V_{\rm cor}$  = -0.735 and  $I_{\rm cor}$  = 6.80 × 10<sup>-4</sup>). Finally, it is important to give an estimate of the cost of electrode fabrication in comparison with the Li-ion battery systems (4-6 USD/Wh). Based on the current market price of related materials, the study here roughly lies on 2 USD/Wh and may be further reduced to 0.5-1 USD/Wh through mass production;<sup>63</sup> first, transfer of CNTs onto a Ni current collector and subsequent oxide deposition can be achieved in a large scale;<sup>38,39</sup> second, Figures 2 and 6 confirm the device reliability and reproducibility.

## 4. CONCLUSIONS

Since charge–discharge processes mainly take place at the solid–liquid interface, the fabrication of electrodes with thick active mass is therefore unnecessary. This study demonstrates the production of high  $C_{s'}$  P<sub>D</sub>, and E<sub>D</sub> on a low active mass electrode where three different energy storage mechanisms synergistically operate. The VN/CNTs/Ni and VN/Ni electrodes are therefore made and tested in two different neutral electrolytes for comparison. The coating of VN nanoparticles onto CNTs significantly improves  $\sigma$ ,  $N_{A'}$   $S_{\text{BET}}$ ,  $R_{d'}$  and  $C_{s'}$  and  $C_{s(\text{el-A})} > C_{s(\text{el-B})}$  is due to lower  $R_s$  and  $R_{\text{ct}}$ . Prolonged coating of VN nanoparticles reduces  $N_A$  and  $S_{\text{BET}}$ , thus giving  $C_{s(\text{VN/CNTs/Ni15})} > C_{s(\text{VN/CNTs/Ni30})}$ . The  $V_{\text{cor}}$  and  $I_{\text{cor}}$  values of CNTs and Ni are very low and are -0.7 and  $7 \times 10^{-4}$ , respectively.

# ASSOCIATED CONTENT

#### Data Availability Statement

Data will be made available on request.

#### **5** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c08313.

EDS profiles of VN, TEM images and CV profiles of VN/CNTs/Ni<sub>30</sub> and VN/CNTs/Ni<sub>15</sub> at different scan rates, power density and energy density of VN/CNTs/Ni and VN/Ni in el-A and el-B, and CV profile of the Ni current collector in el-A (PDF)

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#### Notes

The authors declare no competing financial interest.

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