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Erstveröffentlichung in / First published in:

Nano Energy. 2019, 65, Art. Nr. 103987. ScienceDirect. ISSN 2211-2855.

DOI: <https://doi.org/10.1016/j.nanoen.2019.103987>

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Amino Functionalization Optimizes Potential Distribution: A Facile Pathway Towards High-Energy Carbon-Based Aqueous Supercapacitors

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Abstract

Resolving the mismatch between the practical potential window (PPW) and the available capacitive potential window of supercapacitor electrodes provides a feasible way to expand the operating voltage of supercapacitors, which further boosts energy density. Here, our research unveils a unique approach to manually control the PPW of the corresponding carbon-based supercapacitors (CSCs) by rational functionalization with amino groups. The extra pair of electrons from amino N atoms naturally adsorbs cations in the electrolyte, which rationalizes the surface charge of the carbon electrode and adjusts the PPW. A remarkable voltage expansion is achieved for CSCs, from 1.4 V to its maximum limit, 1.8 V, correspondently resulting in an approximately 1-fold increase in the energy density. Importantly, such a simple strategy endows our CSCs with an outstanding maximum energy density of 7.7 mWh cm⁻³, which is not only among the best values reported for thin-film CSCs but also comparable to those reported for Li thin-film batteries. These encouraging results are believed to bring fundamental insights into the nature of potential control in energy storage devices.

Keywords: supercapacitors, surface functionalization, potential distribution, operating voltage, energy density

1. Introduction

Carbon-based supercapacitors (CSCs) storing charges through fast ionic adsorption/desorption on a carbon surface, can operate at a very high rate and exhibit excellent cycling stability [1-4]. Based on the low mass density and abundant resources of carbon materials, the expanding use of CSCs has attracted significant attention in a growing set of practices, especially for building energy-bursting equipment [5-8]. However, CSCs exhibit rather low energy densities (only $4\text{--}5\text{ Wh kg}^{-1}$, $< 1\text{ mWh cm}^{-3}$) [9-12], making it difficult for them to compete with other energy storage devices. To keep pace with the continuously increasing energy demands, current exploration on CSCs is trending in two different directions: capacitance increase and operating voltage expansion. Significant progress has been made in designing high-capacitance carbon-based electrodes via strategies such as large accessible surface construction, heteroatom doping, and chemical activation [13, 14]. In contrast, only a few efforts have been devoted to expanding the safe operating voltage of CSCs, although this can offer a more efficient pathway to boost the energy density as the energy density is proportional to the square of the voltage.

Constructing CSCs with organic electrolytes represents the most common method to increase the operating voltage due to the high electrolysis resistance of organic electrolytes [11, 15]. However, limited by the relatively low ion diffusion kinetics and high resistance, the high voltage of organic CSCs is accompanied by capacitance and power deterioration. When considering cost, safety, and eco-friendly issues, it is more appealing to employ aqueous electrolytes.[9, 16, 17] In light of the large overpotential for water electrolysis, the available capacitive potential window (CPW) for carbon electrodes in neutral electrolytes is beyond the thermodynamic electrolysis voltage (1.23 V) [9, 18-20]. The barrier faced by aqueous CSCs is that the CPW of the carbon electrode in a neutral electrolyte is still underexploited [10, 21, 22].

This challenge stems from the fact that one electrode tends to first reach the potential limit (onset potential of the hydrogen or oxygen evolution reaction) while CSCs are charged, but there is still a specific potential range on the other electrode side that is not used (Scheme 1a). To address this issue, the use of two carbon electrodes with unequal masses is the most common method, however, this method reduces the specific capacitance [11, 23]. Physical separation of ions was recently applied to enable different pH environments for negative and positive electrodes, which resulted in a high stable voltage of 1.77 V for CSCs [24]. However, the use of ion-exchange membranes complicated the configuration of the CSCs and would severely limit practical applications. To date, it is still of critical importance to further advance the understanding of the potential distribution in CSCs and develop reliable approaches to enlarge the operating voltage.

P_{0V} , which refers to the electrode potential when CSCs operate at 0 V, is an important parameter in determining the practical potential window (PPW) of CSCs [10, 11]. Developing a controllable method to modulate the P_{0V} offers a viable way to rationally adjust the PPW, which would expand the operating voltage without sacrificing the specific capacitance. In this work, we report for the first time a facile strategy to controllably adjust the P_{0V} via functionalization of carbon surfaces with amino groups. It is revealed that amino nitrogen atoms with an extra pair of electrons can function as Lewis-base sites to naturally adsorb cations in an electrolyte and thus alter the surface charge of a carbon electrode (Scheme 1b). By adjusting the number of amino groups, the P_{0V} can be controllably shifted towards negative values, thus solving the mismatch between the PPW and the available CPW of electrodes. As a result, the operating voltage of CSCs can be markedly increased from 1.4 V to its maximum limit, 1.8 V, which yields an approximately 1-fold increase in the energy density. Due to the large voltage and high volumetric capacitance (90.7 F cm^{-3}) of an N-doped hierarchical porous carbon (NHPC)

electrode, the fabricated CSCs deliver a maximum volumetric energy density of 7.7 mWh cm^{-3} , which is significantly higher than those of recently reported thin-film CSCs and comparable with those of Li thin-film batteries.

Scheme. 1 (a) The correlation among the PPW, CPW, and P_{0v} . (b) Amino groups are functionalized on the surface of carbon. Lewis-base nitrogen atoms naturally adsorb cations, enabling the carbon electrode to show features as being negatively charged.

2. Experimental Section

2.1 Materials

All chemicals were of analytical grade and used directly without any purification. Sodium chloride (NaCl), chitosan, acetic acid, potassium hydroxide (KOH), ethylene diamine, 1,2-propane diamine, and 1,3-propane diamine were purchased from Sigma-Aldrich. Hexafluorophosphate azabenzotriazole tetramethyl uronium (HATU), Super P, polyvinylidene fluoride, and N-methyl pyrrolidone were purchased from Alfa Aesar.

2.2 Synthesis of NHPC

1 g of NaCl and 2 mL of acetic acid were firstly dissolved into 48 mL of distilled water. Subsequently, 1 g of chitosan was added into the mixture solution, followed by vigorous stirring until a transparent hydrogel with large viscosity was formed. The obtained hydrogel was frozen by liquid nitrogen, and then dried by a lyophilizer to obtain chitosan/NaCl aerogel. Pyrolysis of the aerogel was performed in N₂ at 800 °C for 2 hours with a heating rate of 3 °C min⁻¹. The carbonized sample was then washed with water to remove NaCl and mixed with 20 mL of KOH solution (1 g KOH). Afterwards, water was evaporated to get the solid composite by drying the sample at 120 °C. The composite was further annealed in N₂ at 800 °C for 2 hours with a heating rate of 3 °C min⁻¹. Finally, the sample was thoroughly washed with distilled water for three times and dried at 80 °C before further characterization.

2.3 Synthesis of amino group-functionalized NHPC

Firstly, ethylene diamine was used to functionalize NHPC with amino groups by a facile amidation reaction catalyzed by HATU. 1 g of HATU was dissolved into 10 mL of ethylene diamine. A certain volume of the mixture solution was mixed with 100 mg of NHPC sample, and then kept at 80 °C for 1 hour. Afterwards, the sample was washed with ethanol and dried at 80 °C. By using different volume of mixture solution (1 mL, 1.5 mL, 2 mL and 4 mL), samples functionalized with different amounts of amino groups were obtained, which are denoted as

NHPC-N1, NHPC-N2, NHPC-N3, and NHPC-N4. Same methods were used to functionalize commercial activated carbon (YP-50F, Kuraray company) with amino groups, which are denoted as YP50-N1, YP50-N2, YP50-N3, and YP50-N4.

Similar methods were also employed to synthesize amino group-functionalized NHPC samples by simply replacing ethylene diamine with 1,2-propane diamine or 1,3-propane diamine. The obtained samples using 1,2-propane diamine are denoted as NHPC-1N1, NHPC-1N2, NHPC-1N3, and NHPC-1N4, while the samples using 1,3-propane diamine are denoted as NHPC-2N1, NHPC-2N2, NHPC-2N3, and NHPC-2N4.

2.4 Electrochemical measurement and calculation

To prepare the electrodes, 5 mg of polyvinylidene fluoride was firstly dissolved into 1 g of N-methyl pyrrolidone, followed by adding 40 mg of our samples and 5 mg of carbon black. After stirring for 6 hours, 20 μL of the slurry was drop casting on a piece of carbon cloth ($1 \times 0.5 \text{ cm}^2$), and the prepared electrodes were dried in an oven at 80°C . The loading mass of active materials is about 2.5 mg cm^{-2} .

The capacitive performance of single electrode was detected in a conventional three-electrode system, employing an electrochemical workstation (CHI 760E). Ag/AgCl electrode and over-capacitance graphite rod were used as reference electrode and counter electrode, respectively. 5 M LiCl aqueous solution was used as electrolyte. Specific capacitances of electrodes were calculated from their CV curves and galvanostatic charge/discharge curves according to equation (1) and (2), where $C_G (\text{F g}^{-1})$ is the gravimetric capacitance, $Q (\text{C})$ is the average charge during the charging and discharging process, $\Delta V (\text{V})$ is the potential window, $m (\text{g})$ is the loading mass

of active material, I (A) is the current, E (V) is the potential, v (V s^{-1}) is the scan rate, and Δt (s) is the discharge time.

$$C_G = \frac{Q}{\Delta V \cdot m} = \frac{\int |I| dE}{2v \cdot \Delta V \cdot m} \quad (1)$$

$$C_G = \frac{I \cdot \Delta t}{\Delta V \cdot m} \quad (2)$$

Devices constructed by two piece of carbon cloth based electrodes were assessed to study the potential distribution by using cyclic voltammetry. An additional Ag/AgCl electrode was inserted into this system to in-situ detect the potential variation of the positive electrode. The potential variation of the negative electrode was obtained according to equation (3), where E_C (V) is the potential of the cathode, E_A (V) is the potential of the anode, and V (V) is the voltage of the CSCs.

$$V = E_C - E_A \quad (3)$$

To study the performance of CSCs based on our sample, free-standing electrode was firstly prepared. In detail, 8 mg of graphene and 32 mg of our sample (NHPC or NHPC-N2) were firstly dispersed in ethanol by sonification for half an hour. Free-standing film was then obtained by vacuum filtration, followed by drying at 80 °C in a vacuum oven. The mass loading and thickness for the film are $2 \pm 0.2 \text{ mg cm}^{-2}$ and $60 \pm 5 \text{ }\mu\text{m}$, respectively. CSCs were then assembled using 2-electrode set-up in Swagelok cells using 8 mm-diameter disks of free-standing electrodes. The specific capacitance of the CSCs was calculated from the slope of the discharge curve using the equation (4), where C_{SCs} (F g^{-1}) is the specific capacitance of the CSCs, I (A) is the applied current, Δt (s) is the discharge time, V (V) is the operating voltage, and m (g) is the mass of active the material. Energy density, and power density of the devices were

obtained according to equation (5) and (6), where E (Wh g⁻¹) is the energy density and P (W g⁻¹) is the power density.

$$C_{SCS} = \frac{I \cdot \Delta t}{V \cdot m} \quad (4)$$

$$E = \frac{1}{2 \times 3600} \cdot C_{SCS} \cdot V^2 \quad (5)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (6)$$

2.5 Characterization.

The microstructures and compositions of samples were analyzed by field emission scanning electron microscope (FESEM, Carl Zeiss Gemini 500), transmission electron microscopy (TEM, FEI Tecnai G² F30), confocal Raman microscope (NT-MDT) with a 532 nm laser, and XPS (XPS, ESCALab250, Thermo VG). The surface area of the sample was calculated from nitrogen adsorption/desorption isotherms at 77 K on a Quantachrome volumetric analyzer. Before measurement, all the samples were outgassed at 120 °C for 10 hours under vacuum situation. Zeta potentials of the samples dispersed in electrolyte were determined with a Zetasizer Nano ZSP (Malvern Instruments, Worcestershire, UK) using the laser Doppler velocimetry technique.

3. Results and Discussion

NHPC was first synthesized via pyrolysis of chitosan/NaCl hybrid aerogel followed by KOH activation. Chitosan is derived from the second most abundant renewable biopolymer, *i.e.*, chitin, and was chosen as the nitrogen-rich precursor[25]. The hydrogel was first prepared by dissolving chitosan in water with acetic acid as a cross-linking agent and NaCl as a pore-creating agent (Fig. 1a). A 3D freestanding chitosan/NaCl aerogel (Fig. 1b) was obtained through lyophilization

and was sequentially carbonized under a nitrogen atmosphere (Fig. 1c). After removing the NaCl template by washing with distilled water, the sample was mixed with KOH and annealed again to generate more micropores. Scanning electron microscopy (SEM, Fig. 1d) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Fig. 1e) images elucidate the 3D porous structure consisting of crumpled carbon thin layers with random orientations. Such interconnected carbon walls offer numerous macropores as favorable open channels, which can accelerate ion diffusion within the carbon matrix to trigger a fast electrochemical response.[26] Additionally, abundant micropores are observed on the surface of the carbon walls by transmission electron microscopy (Fig. S1), and these micropores provide rich accessible sites for ion adsorption.[27]

Fig. 1. (a) Schematic diagram illustrating the chemical structure of cross-linked chitosan. Digital photos of the chitosan/NaCl hybrid aerogel (b) before and (c) after pyrolysis. (d) SEM image, (e) HAADF-STEM image, (f) N 1s XPS spectrum and (g) nitrogen adsorption-desorption isotherm profile of NHPC. The inset of (g) is the pore size distribution of NHPC.

The Raman spectrum (Fig. S2) presents typical D and G bands with a high intensity ratio (I_D/I_G) of 1.2, indicating the low graphitization degree of NHPC.[28, 29] The XPS survey spectrum (Fig. S3a) shows the existence of C, O, and N with atomic percentages of 85.7, 12.3 and 2.0%, respectively, while no other impurity was detected. The N 1s XPS spectrum (Fig. 1f)

elucidates four N-doping configurations in the NHPC sample, namely, pyridinic N at 398.7 eV, amino or amide N at 399.6 eV, pyrrolic N at 400.5 eV, and graphitic N at 401.8 eV. Moreover, apart from sp^2 -hybridized carbon at 284.7 eV, the C-N bond at 285.6 eV and the $\pi-\pi^*$ bond at 293.1 eV, three broad components associated with oxygen account for the overlapping C 1s XPS spectrum, revealing decoration with oxygen-containing functional groups (Fig. S3b)[30, 31]. Importantly, the peak located at 289.0 eV is attributed to carboxyl groups ($O-C=O$), which provide an opportunity for postmodification. Furthermore, a clear steep increase was observed for the nitrogen adsorption-desorption isotherm profile of NHPC at both $< 0.1 P/P_0$ and $0.5-1.0 P/P_0$ (Fig. 1g), implying a hierarchical porous structure containing micro- and macropores. The abundant micropores are also indicated by the pore size distribution analysis using a nonlocal density functional theory (NL-DFT) model, which displays three peaks centered at 1.2 nm, 1.5 nm and 1.8 nm. An excellent specific surface area of $2065 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $1.1 \text{ cm}^3 \text{ g}^{-1}$ are achieved for NHPC (Fig. S4).

To investigate the capacitive properties of NHPC, an NHPC electrode was prepared by coating the sample on carbon cloth and assessing it in a neutral 5 M LiCl electrolyte with a three-electrode system. The linear sweep voltammetry curves presented in Fig. 2a show that the onset potentials for the HER and OER are -0.8 and 1.0 V vs. Ag/AgCl. These two potentials are commonly regarded as the lower and upper limits for the available CPW of the NHPC electrode, which also agree well with the step potential tests (Fig. S5). Cyclic voltammetry (CV) curves of the NHPC electrode obtained in the potential range of $-0.8 \sim 1.0 \text{ V vs. Ag/AgCl}$ display nearly rectangular shapes, which are representative of typical electrical double layer capacitive behavior (Fig. 2b). The electrode exhibits a specific capacitance of 194 F g^{-1} at 5 mV s^{-1} and 195 F g^{-1} at 1 A g^{-1} (Fig. S6), and these values are better than those of the reported carbon electrodes tested in

neutral electrolyte [1, 5, 9, 32-39] (Table S1). Even at a high scan rate of 600 mV s^{-1} , the capacitance is still 105 F g^{-1} , suggesting excellent rate capability.

Fig. 2. (a) Linear sweep voltammetry curves of the NHPC electrode at 5 mV s^{-1} . (b) CV curves of the NHPC electrode at various scan rates. (c) Potential distribution of NHPC electrode-based CSCs when charged/discharged at different voltages. (d) Digital photo of the positive electrode after the CV test of CSCs with a voltage of 1.8 V.

Next, the relationship between the CPW and PPW of the NHPC-based two-electrode device was investigated. The respective potential variation of the two electrodes during the charge/discharge process of the CSCs was monitored in situ with an additional Ag/AgCl reference electrode. Fig. 2c illustrates the potential distribution of the negative and positive electrodes when the device was charged/discharged with a gradually increasing voltage (Fig. S7).

Notably, the potential of the positive electrode reaches the upper limit (*i.e.*, 1.0 V *vs.* Ag/AgCl) when the operating voltage is only 1.4 V. This indicates that the maximum operating voltage of the fabricated CSCs can only be 1.4 V. Compared with the whole CPW of 1.8 V, a potential range of 0.4 V is not used. Obvious gas bubbles were observed on the surface of the positive electrode during charging/discharging with a voltage of 1.8 V, which suggests oxygen evolution (Fig. 2d). Moreover, the P_{0V} of the CSCs, the cutoff potential for the negative and positive electrodes, remains almost the same (0.33 V *vs.* Ag/AgCl), even though the operating voltage changed from 1.2 to 1.8 V. That's because P_{0V} mainly depends on the open circuit potential of two electrodes, and the voltage of device doesn't affect the initial surface charge of the electrode. Inspired by the above discussion, it is believed that a further expansion of the operating voltage can be realized by negatively shifting the P_{0V} .

Since the P_{0V} highly depends on the surface charge condition, it is hypothesized that the P_{0V} can be negatively shifted by introducing a carbon electrode with substituents possessing cation-adsorption properties. Therefore, NHPC was functionalized with amino groups (-NH/-NH₂) through a facile amidation reaction between the carboxyl groups on the NHPC surface and ethylene diamine (Fig. S8). By adjusting the ratio of ethylene diamine to NHPC, samples functionalized with different amounts of amino groups were synthesized, which are denoted as NHPC-N1, NHPC-N2, NHPC-N3, and NHPC-N4. In comparison with pristine NHPC, the samples after functionalization show other characteristic infrared absorption peaks, including a peak at 3303 cm⁻¹ indexed to N-H stretching vibrations, peaks at 1563 and 1637 cm⁻¹ associated with the amide I and II bands, respectively, and multiple peaks located at 400-1300 cm⁻¹ attributable to the fingerprint of an alkyl chain[40, 41] (Fig. S9). The N 1s XPS spectra (Fig. 3a) were used to trace the variation in the surface N atoms. Along with the increasing ratio of

ethylene diamine to NHPC, the atomic percentage of N among all atoms undergoes an upward trend (2.0% for NHPC to 4.1% for NHPC-N1, 6.1% for NHPC-N2, 6.6% for NHPC-N3, and 7.2% for NHPC-N4). The atomic percentage of amino and amide N among all N atoms was estimated by deconvoluting the N 1s XPS spectra into the pyridinic N, amino/amide N, pyrrolic N, and graphitic N components (Fig. S10). As expected, the percentage of amino/amide N also increased (9.5% for NHPC, 25.2% for NHPC-N1, 37.5% for NHPC-N2, 47.1% for NHPC-N3, and 47.6% for NHPC-N4), which further supports the successful functionalization of carbon electrodes with ethylene diamine species.

Fig. 3. (a) The atomic percentage of N among all atoms (up) and the atomic percentage of amino/amide N among all N atoms (down) in NHPC, NHPC-N1, NHPC-N2, NHPC-N3, and NHPC-N4. (b) Electrode potential distribution of NHPC, NHPC-N1, NHPC-N2, NHPC-N3, and NHPC-N4-based CSCs when they operate at 1.8 V. (c) CV curves of NHPC-CSCs and NHPC-N2-CSCs at 10 mV s⁻¹. (d) Gravimetric capacitances of NHPC-N2-CSCs and NHPC-N2 electrode. (e) Gravimetric Ragone plots of NHPC-CSCs and NHPC-N2-CSCs. (f) Volumetric

Ragone plots of NHPC-CSCs and NHPC-N2-CSCs in comparison with those values reported from carbon-based thin-film CSCs [12, 42-45] and Li thin-film batteries [46]. These values are calculated by taking the whole volume of the device into account.

Fig. 3b and S11 display the potential distribution of the two-electrode device based on different electrodes when they are charged/discharged with an operating voltage of 1.8 V. It is revealed that the P_{0V} is negatively shifted with the increasing amount of amino/amide N. For the optimal case, the PPW of the device based on the NHPC-N2 electrode is the same as the available CPW for the NHPC-N2 electrode. As expected, no bubble was observed on the surface of the NHPC-N2 electrodes during the electrochemical tests (Fig. S12), indicating that the unfavorable oxidation reaction on the positive electrode was effectively suppressed. Therefore, we conclude that CSCs constructed by NHPC-N2 should reach a high operating voltage of 1.8 V.

Furthermore, NHPC-N2-based CSCs (NHPC-N2-CSCs) were constructed using two free-standing NHPC-N2 films (42 μm in thickness, digital photo and SEM images are shown in Fig. S13 and Fig. S14) sandwiched with a separator (25 μm in thickness). NHPC-based CSCs (NHPC-CSCs) were also assembled for comparison. Under the operating voltage of 1.8 V, a sharp oxidation current increase was observed for NHPC-CSCs during the anodic scan (Fig. 3c), which was associated with the irreversible oxidation reactions. In contrast, NHPC-N2-CSCs exhibited an ideal capacitive performance, as demonstrated by the nearly rectangular CV profile. This result highlights the successful voltage expansion for NHPC-N2-CSCs compared to that for NHPC-CSCs. Fig. S15 displays the triangle galvanostatic charge/discharge (GCD) curves of NHPC-N2-CSCs. At a current density of 1 A g^{-1} , the gravimetric capacitance of NHPC-N2-CSCs is calculated to be 45.3 F g^{-1} , corresponding to a specific capacitance of 181.2 F g^{-1} (volumetric capacitance of 90.7 F cm^{-3}) for the NHPC-N2 free-standing electrode (Fig. 3d). An

excellent rate performance was manifested by the high capacitance retention of 58% as the discharge current density increased by 10 folds. The CSCs operated at 1.8 V also showed excellent cycling stability with a capacitance loss of only 5.5% after 10000 charge/discharge cycles (Fig. S16). XPS spectra was performed for NHPC-N2 electrode after cycling stability test to assess the surface chemistry change. As revealed by the N 1s XPS spectrum (Fig. S17), NHPC-N2 electrode after cycling stability tests can maintain most of the amino N, indicating the functionalized amino groups are stable during cycling stability test.

On the other hand, GCD curves of NHPC-CSCs were also collected with an operating voltage of 1.4 V (Fig. S18). Ragone plots (Fig. 3e) were further calculated according to the GCD curves and are compared with those of state-of-the-art SCs (Fig. S19). Remarkably, when the operating voltage increases from 1.4 to 1.8 V, the NHPC-N2-based CSCs nearly doubles the energy density (*e.g.*, 20.4 Wh kg⁻¹ vs. 10.6 Wh kg⁻¹ for NHPC-N2 vs. NHPC at 1 A g⁻¹) without sacrificing the power density (900 W kg⁻¹ vs. 700 W kg⁻¹). The maximum volumetric energy density of NHPC-CSCs is 4.0 mWh cm⁻³ at a power density of 0.27 W cm⁻³ (the device volume is illustrated in Fig. S20), which is among the highest reported values for thin-film aqueous CSCs, such as reduced graphene oxide (rGO) CSCs (0.16 mWh cm⁻³),^[42] laser-scribed graphene (LSG) CSCs (0.07 mWh cm⁻³),^[12] sulfur-doped graphene (SG) CSCs (3.0 mWh cm⁻³),^[43] and fluorine-modified graphene (FG) CSCs (3.7 mWh cm⁻³),^[44] and even substantially higher than those of many organic CSCs such as LSG ionic-liquid CSCs (1.5 mWh cm⁻³)^[12] and screen-printed graphene (SPG) ionic-liquid CSCs (1.9 mWh cm⁻³)^[45]. Moreover, in light of the enlarged voltage, NHPC-N2-CSCs also deliver an excellent volumetric energy density of 7.7 mWh cm⁻³ at 0.34 W cm⁻³, making them potentially competitive against Li thin-film batteries (0.2 – 7.2 mWh cm⁻³)^[46].

Fig. 4. (a) Zeta potential of all the samples dispersed in a 5 M LiCl solution. (b) Schematic illustration of different doping N atoms and their corresponding binding energies with (c) H⁺ or (d) Li⁺.

It is well accepted that when one electrode is negatively charged, its surface attracts the cations in the electrolyte, forming an electrical double layer. Similarly, the functionalized species with a Lewis-base feature function as electron donors to guide the natural adsorption of cations, which thus regulate the surface charge of the electrode. Therefore, the P_{OV} can be controllably tuned by decorating the carbon material with cation-adsorption species. The adsorption of cations on the amino-functionalized NHPc samples was verified by their zeta potential in a 5 M LiCl electrolyte. As shown in Fig. 4a, the pristine NHPc sample depicts a slightly negative zeta potential of -0.23 mV. After functionalization with amino groups, the samples show increasing

zeta potentials as the number of functionalized amino groups increases (in detail, 1.24 mV for NHPC-N1, 2.20 mV for NHPC-N2, 2.41 mV for NHPC-N3, and 3.20 mV for NHPC-N4).

Density functional theory (DFT) calculations were carried out to understand the binding behavior between different N dopants (Fig. 4b and S21) and cations (H^+ and Li^+) in the electrolyte. As shown in Fig. 4c and 4d, the binding strength with H^+ for various N species follows the order pyridinic N (-0.90 eV) > amino N (0.86 eV) > pyrrolic N (1.66 eV) > graphitic N (1.95 eV), while the order for Li^+ adsorption is pyridinic N (-2.90 eV) > amino N (-2.75 eV) > graphitic (-2.21 eV) > pyrrolic N (-2.06 eV). Clearly, the adsorption capability of pyridinic N and amino N are significantly higher than those of pyrrolic N and graphitic N. In addition, N atoms in the ethylene diamine species (denoted as N5 and N6 in Fig. 4b, 4c and 4d) exhibit strong binding energies with H^+ of 0.50 and -0.22 eV and with Li^+ of -2.76 eV and -2.96 eV. These values are comparable with those for the pyridinic N and amino N.

In addition to ethylene diamine, 1,2-propane diamine and 1,3-propane diamine were also used to functionalize NHPC with amino groups. By controlling the ratio of these organic amines, P_{0V} adjustment and voltage expansion were realized (Fig. S22 and S23). In addition, such an amino functionalization approach is also effective for adjusting the P_{0V} of CSCs based on commercial capacitive carbon materials (such as YP-50F, Kuraray, Fig. S24). After optimization, the energy density significantly increased from 6.8 Wh kg^{-1} to 13.9 Wh kg^{-1} at a discharge current density of 1 A g^{-1} . All these results suggest the generality of employing cation-adsorption amino groups to expand the operating voltage and enhance the energy density of CSCs.

4. Conclusion

In summary, we report a novel strategy for controllably adjusting the P_{0V} of CSCs by functionalizing a carbon electrode with cation-adsorption amino groups. Through such an approach, the operating voltage of CSCs achieves a remarkable expansion from 1.4 V to 1.8 V, which further results in a 1-fold increase in the energy density (maximum energy density of 20.4 Wh kg⁻¹ and 7.7 mWh cm⁻³). The importance of this study resides in the improvement of the energy density for CSCs through facile surface functionalization of the electrode, rather than complicated electrode/device design. The obtained understanding fills the knowledge gap regarding the nature of potential control in supercapacitors and will inspire efficient design of high-voltage aqueous energy storage devices.

Supporting Information.

Supplementary data associated with this article can be found in the online version.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 785219, the Initiative and Networking Fund of the German Helmholtz Association, Helmholtz International Research School for Nanoelectronic Networks NanoNet (VH-KO-606), HIPER-G, and EU Graphene Flagship. This work is also supported by the German Research Foundation (DFG) within the Cluster of Excellence 'Center for Advancing Electronics Dresden' (cfaed). M. Yu is grateful for a scholarship from the Alexander von Humboldt Foundation. The authors also thank Dr. Jian Zhang, Dr. Hanjun Sun, and Guangbo Chen (TU Dresden) for helpful discussions. The authors acknowledge the use of the facilities in the Dresden Center for Nanoanalysis at the Technische Universität Dresden.

Conflict of Interest

The authors declare no competing financial interest.

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A facile pathway to control the practical potential windows of carbon-based supercapacitors is unveiled by rational functionalization with amino groups. The proposed strategy enables a remarkable voltage expansion, from 1.4 V to its maximum limit, 1.8 V, correspondently resulting in the doubled energy density for our carbon-based supercapacitors.