Defect-Engineered Nanostructured Ni/MOF-Derived Carbons for an Efficient Aqueous Battery-Type Energy Storage Device

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ABSTRACT: A Ni-based metal–organic framework (Ni-MOF) has been synthesized using a microwave-assisted strategy and converted to nanostructured Ni/MOF-derived mesoporous carbon (Ni/MOFDC) by carbonization and acid treatment (AT-Ni/MOFDC). The materials are well characterized with Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET), revealing that chemical etching confers on the AT-Ni/MOFDC-reduced average nanoparticle size (high surface area) and structural defects including oxygen vacancies. AT-Ni/MOFDC displays low series resistances and a higher specific capacity (C) of 199 mAh g⁻¹ compared to Ni/MOFDC (92 mAh g⁻¹). This study shows that the storage mechanism of the Ni-based electrode as a battery-type energy storage (BTES) system can be controlled by both non-faradic and faradic processes and dependent on the sweep rate or current density. AT-Ni/MOFDC reveals mixed contributions at different rates: 75.2% faradic and 24.8% non-faradic contributions at 5 mV s⁻¹, and 34.1% faradic and 65.9% non-faradic at 50 mV s⁻¹. The full BTES device was assembled with AT-Ni/MOFDC as the cathode and acetylene black (AB) as the anode. Compared to recent literature, the AT-Ni/MOFDC/AB BTES device exhibits high energy (33 Wh kg⁻¹) and high power (983 W kg⁻¹) with excellent cycling performance (about 88% capacity retention over 2000 cycles). This new finding opens a window of opportunity for the rational designing of next-generation energy storage devices, supercapatteries, that combine the characteristics of batteries (high energy) and supercapacitors (high power).

INTRODUCTION

With the ever-growing global energy demand, coupled with the emergence of the fourth Industrial Revolution, it has become increasingly important to develop clean, affordable, and sustainable electrochemical energy storage devices.¹ Electrochemical energy storage (EES) systems that combine the properties of batteries (high energy) and supercapacitors (high power) are needed to power the next-generation energy-hungry applications, including portable electronics, pure and hybrid electric vehicles, and trains.²,³

EES can broadly be categorized into three types, based on their energy storage mechanisms:⁴ (i) electric double-layer capacitive (EDLC) charge storage, (ii) pseudocapacitive charge storage, and (iii) battery-type charge storage. In summary, EDLC uses only carbons (such as carbon black) as its electrodes, stores charge by a simple ion-adsorption process at the electrode/electrolyte interface,⁵ and exhibits rectangular-shaped cyclic voltammograms. EDLC is a purely capacitive/non-faradic process (i.e., surface-controlled kinetics). Pseudocapacitors mostly use transition metal oxides or conducting polymers and store charge via non-faradic and faradic (diffusion-controlled kinetics) processes,⁶ and they exhibit symmetric redox peaks (i.e., peak-to-peak separation, ΔEₚ, being essentially zero voltage). Pseudocapacitive storage is a surface-confined redox process, and the storage mechanism can be controlled by both faradic (diffusion-controlled kinetics) and non-faradic (surface-controlled kinetics) processes. On the other hand, battery-type energy storage (BTES) is characterized by the bulk redox (ion intercalation) process, exhibits asymmetric redox peaks (i.e., ΔEₚ being greater than zero voltage), and is said to be fully controlled by the faradic process (diffusion-controlled kinetics),⁷ a statement which this present work disagrees with; it is not all faradic (to be discussed later). The fourth categorization which is gaining ground in the literature is called battery-supercapacitor hybrid or hybrid energy storage system (HESS) or supercapattery or supercabattery, which describes an energy storage device that...
combines the properties of an EDLC (i.e., high power density) and battery (i.e., high energy density).

Battery-type cathode materials, especially Ni-based materials, are high-voltage materials compared to carbons used in the conventional EDLCs. Some authors still refer to battery-type Ni-based electrodes as pseudocapacitors and continue to carry out the calculation of energy storage in capacitance (Farad) rather than capacity (mAh). This misinterpretation has continued to generate some concern to researchers in the electrochemical energy storage community, as it makes it very difficult for one to reasonably compare electrochemical data with literature. Another concern that one observes in the literature is the generalization that the charge storage in BTES is a purely diffusion-controlled (faradic) process, with no significant contribution to the energy storage mechanism by the capacitive process. Thus, it is critical to establish if the energy storage mechanism of every Ni-based electrode (well known for its capacitive process with a negligible capacitive contribution. It is this knowledge gap in the battery-type energy properties of Ni-based electrode materials that motivated us to explore the electrochemistry of Ni-metal–organic framework (MOF)-based electrode materials as a BS system.

MOFs have continued to attract tremendous research attention due to their inherent tunable pore sizes, highly accessible surface areas, active metal sites, and ordered crystallinity. The good properties of MOFs make them useful for a variety of applications, including supercapacitors. Direct carbonization of the MOFs represents an effective strategy for making porous carbon materials with increased surface areas, uniform pore size distributions, and improved electrical conductivity. Thus, MOF-derived carbons (MOFDC) are important electrodes for the development of supercapacitors.

In this work, a microwave-assisted synthesis strategy has been used to prepare a Ni-based MOF (Ni-MOF) as a sacrificial template for the preparation of nanostructured Ni-supported MOFDC (Ni/MOFDC) by carbonization and subsequently acid-treated to give AT-Ni/MOFDC. Chemical etching was purposely carried out to tune the physicochemical properties of the Ni nanoparticle-based composites for enhanced energy storage. It is proved that the chemical etching confers on the Ni/MOFDC defect-rich properties, including the generation of oxygen vacancies, that double its ability to store energy. Importantly, it is proved that the BTES mechanism, in contrast to recent literature, is a mixed faradic/non-faradic process rather than just faradic.

## RESULTS AND DISCUSSION

### Physical Characterization

The Fourier transform infrared (FTIR) spectrum of the as-synthesized Ni-MOF (see Supporting Information, Figure S1a) shows the functional groups present in the formation of the sacrificial template. Absorption of the following functional groups confirms the formation of the as-synthesized Ni-MOF: –OH stretching (3320 cm\(^{-1}\)), C–H stretching (2925 cm\(^{-1}\)), C–H bending (2865 cm\(^{-1}\)), C–H in-plane (869 cm\(^{-1}\)), C–H out-of-plane (1047 cm\(^{-1}\)), C–C stretching (1427 cm\(^{-1}\)), COO\(^-\) symmetric vibrations (1568 cm\(^{-1}\)), CO bending vibrations (704 cm\(^{-1}\)), COO\(^-\) asymmetric vibrations (1365 cm\(^{-1}\)), CO stretching vibration (1726 cm\(^{-1}\)), and Ni–O coordinate bond (548 cm\(^{-1}\)) (18–22). After carbonization and/or chemical etching, the FTIR spectra (see Figure S1b in Supporting Information) show the same functional groups in Ni/MOFDC and AT-MOFDC, which are Ni–O (548 cm\(^{-1}\)), C–C (2025.5 cm\(^{-1}\)), C=\(\text{N}\) (2168.8 cm\(^{-1}\)), carboxylic acid O–H (2363.4–2680.0 cm\(^{-1}\)), C–H bending (2946.2 cm\(^{-1}\)), and C–H stretching (3100.0 cm\(^{-1}\)), respectively. These results show that the frameworks of the MOF were broken down at high temperature.

The Raman spectra of Ni/MOFDC and AT-Ni/MOFDC (Figure 1a) reveal their bond vibrations. In Ni/MOFDC, the bond vibrations of Ni–OH (487 cm\(^{-1}\)), and prominent D (1350 cm\(^{-1}\)), G (1599 cm\(^{-1}\)), and 2D bands (2450 cm\(^{-1}\)) of MOFDC (23). After chemical etching (AT-Ni/MOFDC), the Ni–OH becomes flat with slight shifts in the D band (1345 cm\(^{-1}\)) and G band (1589 cm\(^{-1}\)), whereas the 2D band (2450 cm\(^{-1}\)) remains in the same position. These observations indicate the removal of the passive Ni(OH)\(_2\) layer and create some defects in the chemically etched sample. The removal of the passive Ni(OH)\(_2\) layer is necessary because Ni(OH)\(_2\) has previously been reported to exhibit significant interfacial resistance toward electron transport. To affirm the defects caused by the chemical etching, spectral fitting of both Ni/MOFDC and AT-Ni/MOFDC materials was ensured. The Raman spectra of both materials showed five characteristic bands at approximately 1229, 1343, 1489, 1575, and 1610 cm\(^{-1}\), which corresponded to the D\(_p\), D\(_\text{g}\), D\(_\text{g}\), G, and D\(_2\) bands, respectively (summary in Table S1). The I\(_\text{D}]/I\_\text{G}\) values of the Ni/MOFDC and AT-Ni/MOFDC composites were calculated as 1.8 and 2.1, respectively, following the method employed previously. The increased I\(_\text{D}]/I\_\text{G}\) value of the AT-Ni/MOFDC composite implies that significant defects are created in its arrays.

The crystalline structures of the as-synthesized Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC are studied using powder X-ray...
diffraction (XRD, Figure 1b). The as-synthesized Ni/MOF gives two distinct diffraction patterns at 9.7 and 22.2° corresponding to the Miller indices of Ni-MOF (100) and Ni-MOF (101), respectively. These characteristic peaks are a clear indication for the complete synthesis of the as-synthesized Ni-MOF, and similar diffraction patterns have previously been reported for Ni-based MOFs. After annealing at high temperature, the frameworks of the as-synthesized Ni-MOF decomposed to produce nickel nanoparticles-supported MOF-derived carbon (Ni/MOFDC) with different diffraction patterns observed at 26.3, 44.9, 52.1, 76.7, 93.1, and 98.5°, attributable to broad hexagonal graphitic carbon, MOFDC (002), Ni(111), Ni(200), Ni(220), Ni(311), and Ni(222), respectively. After the chemical etching of Ni/MOFDC to give AT-Ni/MOFDC, the hexagonal graphitic carbon peak became more significant and Ni diffraction patterns were broader, suggesting defect creation in the chemically etched composite and the removal of the passive Ni(OH)₂ layer. This observation corroborates the Raman spectra (Figure 1a), as explained previously.

The chemical nature of the composites before and after chemical etching are investigated using X-ray photoelectron spectroscopy (XPS) (Figure 2), which reveals that the composites consist mainly of Ni, C, and O, and their deconvolutions explain their chemical environment. The Ni 2p of Ni/MOFDC (Figure 2a) was deconvolved into doublets of metallic Ni and Ni(OH)₂, leading to four distinct spectra at binding energies 878.5 eV (Ni(OH)₂ 2p₁/₂ satellite), 872.8 eV (Ni 2p₁/₂), 860.7 eV (Ni(OH)₂ 2p₃/₂ satellite), and 855.1 eV (Ni 2p₃/₂). AT-Ni/MOFDC (Figure 2b) was also fitted to four distinct spectra at 876.0 eV (Ni 2p₁/₂ shake-up satellite), 869.7 eV (Ni 2p₁/₂), 856.8 eV (Ni 2p₃/₂ shake-up satellite), and 853.2 eV (Ni 2p₃/₂). The local variations of the Ni 2p in the composites confirm that Ni/MOFDC has additional Ni(OH)₂ (3p₁/₂ and 3p₃/₂) satellites, while the shift of these spectra in the chemically etched sample reveals the removal of the passive Ni(OH)₂ satellite and its replacement with metallic Ni (3p₁/₂ and 3p₃/₂) shake-up satellites. Also, slight shifts of the Ni (3p₁/₂ and 3p₃/₂) for AT-Ni/MOFDC to lower binding energies confirm the formation of mainly metallic Ni nanoparticles due to the induction of oxygen vacancies (Oᵥ) and strong interaction between Ni and C, leading to increased electron density for the Ni, relative to Ni/MOFDC having additional Ni(OH)₂ satellites, which would have caused the higher binding energies of the Ni (2p₁/₂ and 2p₃/₂) with reduced electron density. The C 1s of Ni/MOFDC (Figure 2c) was fitted into different peaks at binding energies of 287 eV (O=C=N), 285 eV (C=O), 284.6 eV (C sp²/sp³), and 282.2 eV for metallic carbide (Ni–C). The metallic Ni nanoparticles are suspected to remain in the core of the carbon lattice after carbonization of the Ni-MOF sacrificial template, thus preventing the exposure of the metallic
Figure 2d shows similar C 1s deconvolution for AT-Ni/MOFDC, except the metallic carbide spectrum at 282.2 eV, which became flat. This explains that chemical etching does not only create some defects and strains in the Ni lattice but also in the C lattice, as well as removes the passive Ni(OH)$_2$. Interestingly, the deconvoluted O 1s of Ni/MOFDC (Figure 2e) shows two distinct spectra at 532.8 eV (surface oxygen, $O_s$) and 530.5 eV (lattice oxygen, $O_l$), significantly ascribed to the surface coverage of OH on the Ni metals and the Ni–O bond in the sample. These results confirmed the formation of passive Ni(OH)$_2$ on the metallic Ni.

Figure 2f shows the deconvolved O 1s for AT-Ni/MOFDC with only a single peak at 531.9 eV (oxygen vacancy, $O_v$) and a shoulder at 530.5 eV ($O_l$), but the surface coverage of OH became flat, which is similar to the previous report. These results confirm that chemical etching does not only remove the passive Ni(OH)$_2$, but also induces enriched oxygen vacancies in AT-Ni/MOFDC. This observation agrees with the previous reports that etching induces oxygen deficiencies in transition metal oxides/hydroxides.

The nanoparticle morphology of the as-synthesized Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC is studied using transmission electron microscopy (TEM) (Figure 3). The TEM micrograph of the as-synthesized Ni-MOF (see Supporting Information, Figure S2) shows interconnecting core Ni nanoparticles dispersed within the frameworks. However, after annealing at high temperature (900 °C), the frameworks decompose to form Ni/MOFDC (Figure 3a), where the Ni and passive layers of Ni(OH)$_2$ are closely packed on MOFDC with some agglomerations. The chemical etching of the annealed product yielded AT-Ni/MOFDC (Figure 3b), where the passive Ni(OH)$_2$ layers have been removed, leaving behind more active metal Ni-nanoparticles-supported MOFDC with well-dispersed nanoparticles. The Ni nanoparticle size distributions of the Ni/MOFDC and AT-Ni/MOFDC composites are presented in Figure 3c,d, with mean particle sizes of 13.7 and 11.6 nm, respectively. These results further support that chemical etching does not only remove the passive layer of Ni(OH)$_2$ but also slightly reduces the Ni nanoparticle sizes and increases the surface area, which provides more adsorption sites for the OH$^-$ ions with a facile redox reaction and is advantageous in energy storage applications.

The flake-like morphology of the as-prepared Ni/MOFDC and AT-Ni/MOFDC composites is revealed by the scanning electron microscopy (SEM) images (Figure S3a,b, in Supporting Information). The qualitative elemental analysis of the composites was further explained using the coupled energy dispersive X-ray spectroscopy (EDX). As seen, the EDX spectra of the Ni/MOFDC (Supporting Information, Figure S3c) and AT-Ni/MOFDC (Supporting Information, Figure S3d) composites display the following elements: Ni, C, O, N, and Au. The absorption of Au is due to the coating to avoid charging of the samples. Also, absorption of Cl in AT-Ni/MOFDC can be traced to the HCl used for chemical etching.

The surface areas, pore sizes, and pore volumes of the as-prepared Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC composites were verified with the Brunauer–Emmett–Teller (BET) analysis (Table 1). The as-prepared Ni-MOF exhibits the highest pore size but lowest pore volume and surface area. After carbonization, the frameworks decomposed to Ni/MOFDC with reduced pore size but increased pore volume and surface area. Chemical etching led to the increased pore size, pore volume, and surface area of AT-Ni/MOFDC.

**Table 1. Brunauer–Emmett–Teller (BET) Analysis of the As-Prepared Ni-MOF and the Composites**

| samples | pore size/nm | pore volume/cm$^3$ g$^{-1}$ | $S_{BET}$/m$^2$ g$^{-1}$ |
|---------|-------------|-----------------------------|-------------------------|
| Ni-MOF  | 7.1670      | 0.0490                      | 85.0948                 |
| Ni/MOFDC| 2.9493      | 0.1049                      | 148.9240                |
| AT-Ni/MOFDC | 3.4873 | 0.1240                      | 153.0463                |

**Electrochemical Measurements. Three-Electrode System.** The electrochemical performance of the Ni-MOFDC and AT-Ni/MOFDC electrodes was studied in a three-electrode cell using a 3.0 M KOH solution as the electrolyte. As shown in...
and AT-Ni/MOFDC for the three-electrode system. It seems that the tuning of the physicochemical properties of AT-Ni/MOFDC increased surface area (BET analysis, Table 1), among other mean Ni nanoparticle size (TEM analysis, Figure 3d), and similar reports for Ni-based electrodes.44

The area under the CV curve of AT-Ni/MOFDC is greater compared to the pristine counterpart. Furthermore, the GCD curves (Figure 4b) of Ni/MOFDC and AT-Ni/MOFDC show that the redox peaks increase with increasing scan rate (see Supporting Information, Figure S4a,b), which is a typical signature of the electrochemistry of Ni-based electrodes.45 The increase in the peaks’ anodic and cathodic current responses confirms the facile diffusion of the OH− ions.18 The GCD of the electrode materials at different current densities are shown in Figure S4c,d (Supporting Information). The GCD curves of AT-Ni/MOFDC (Figure S4d) are asymmetrical, which is a characteristic of battery-type nanostructured Ni-based electrode materials.

For AT-Ni/MOFDC that contains mainly metallic nickel (Ni0), the metal first undergoes a reduction reaction in alkaline to form nickel hydroxide (Ni(OH)2). This redox behavior of the nanostructured Ni electrode is similar to previous reports.45−47 The area under the CV curve of AT-Ni/MOFDC is greater than that of Ni/MOFDC, which is a clear indication that the etched Ni-based material gives higher specific capacity (Cs) compared to the pristine counterpart.

Figure 4a, the cyclic voltammetry (CV) curves for both Ni/MOFDC and AT-Ni/MOFDC exhibit a redox couple at 5 mV s−1, indicating the battery-like behavior of the materials (faradic redox reactions). The reaction mechanism follows mainly a one-electron transfer process between the divalent and trivalent nickel (Ni2+/Ni3+) in β-type crystals, with the intercalation and deintercalation of OH− ions (eq 1), which is in agreement with similar reports for Ni-based electrodes.14

\[
\beta - \text{Ni(OH)}_2 \xrightarrow{\text{charge}} \beta - \text{NiOOH} \tag{1}
\]

For AT-Ni/MOFDC that contains mainly metallic nickel (Ni0), the metal first undergoes a reduction reaction in alkaline to form nickel hydroxide (Ni(OH)2). This redox behavior of the nanostructured Ni electrode is similar to previous reports.45−47 The area under the CV curve of AT-Ni/MOFDC is greater than that of Ni/MOFDC, which is a clear indication that the etched Ni-based material gives higher specific capacity (Cs) compared to the pristine counterpart.

Furthermore, the GCD curves (Figure 4b) of Ni/MOFDC and AT-Ni/MOFDC were analyzed with the view to establish their charge-storage properties. At the same current density, AT-Ni/MOFDC showed longer discharging time, which corroborates the CV curves. Figure 4c shows the gravimetric capacity of both electrode materials calculated from the CV curves. According to eq 10, the prepared electrodes exhibit a cyclic gravimetric capacity (Cs) of 92 and 199 mAh g−1 at 5 mV s−1 for Ni/MOFDC and AT-Ni/MOFDC, respectively. The higher Cs value of AT-Ni/MOFDC is attributed to its fine-tuned physicochemical properties such as defect creation (Raman analysis, Figure 1a), enriched oxygen vacancy and removal of passive Ni(OH)2 (XPS analysis, Figure 2), reduced mean Ni nanoparticle size (TEM analysis, Figure 3d), and increased surface area (BET analysis, Table 1), among other beneficial properties for energy storage systems. Indeed, it seems that the tuning of the physicochemical properties of AT-Ni/MOFDC as performed in this work provides enough surface area that allows for faradic reactions and facile OH− ion diffusion. This was confirmed by cycling both Ni/MOFDC and AT-Ni/MOFDC materials at different scan rates. Both Ni/MOFDC and AT-Ni/MOFDC show that the redox peaks increase with increasing scan rate (see Supporting Information, Figure S4a,b), which is a typical signature of the electrochemistry of Ni-based electrodes.45−46 The increase in the peaks’ anodic and cathodic current responses confirms the facile diffusion of the OH− ions.18 The GCD of the electrode materials at different current densities are shown in Figure S4c,d (Supporting Information). The GCD curves of AT-Ni/MOFDC (Figure S4d) are asymmetrical, which is a characteristic of battery-type nanostructured Ni-based electrode materials.

Electrochemical impedance spectroscopy (EIS) represents an important tool for analyzing the electrochemical properties of different materials.49−55 Figure 4d shows the EIS measurements of Ni/MOFDC and AT-Ni/MOFDC with an electrical equivalent circuit (EEC, Figure 4d, inset). The Nyquist plot is modeled with the combined Randles circuit (RC) comprising the solution/electrolyte (Rf), the interfacial resistance (Rint) due to IR drop, the charge-transfer resistance (Rct) due to electron transport, the double-layer capacitance (Cd), constant phase element (CPE) due to the inhomogeneity of the electrode surface, and Warburg diffusion region (Zw) describing the resistance to ion diffusion. The impedance of the CPE (Zcpe) is a power law relationship eq 2.51−55

\[
Z_{\text{CPE}} = |Q(\omega^a)|^{-1} \tag{2}
\]

where Q is the frequency-independent constant associated with the electrode/electrolyte interface, j = \sqrt{−1}, ω represents the radial frequency, and the exponent a is the slope of the log Z versus log ω, the values of which are −1 ≤ a ≤ 1: when a = 0, the CPE is a pure resistor; when a = 1, the CPE is a pure capacitor; when a = −1, the CPE is an inductor; and when a = 0.5, the CPE is equivalent to the Warburg impedance (Zw). The Nyquist plots show a larger semicircle diameter for Ni/
MOFDC, indicating decreased faradic reactions at the surface of the active material. Moreover, AT-Ni/MOFDC shows a smaller semicircle indicating low charge-transfer resistance. Interestingly, it can be seen that the semicircle of the AT-Ni/MOFDC material is accompanied by a well-defined 45° line region, which is the signature of a true battery-type energy storage.4

From Table 2, the series resistance \( (R_s + R_{\text{int}} + R_{\text{ct}}) \) values of Ni/MOFDC and AT-Ni/MOFDC are deduced as \( \sim 126 \) and 39 \( \Omega \), respectively. Based on these results, it is observed that AT-Ni/MOFDC has a lower series resistance value, which is a clear indication that it exhibits better conductivity due to its exposed porous carbon and defect of the more active metallic Ni, whereas the increased series resistance of Ni/MOFDC may be traced to the presence of the passive Ni(OH)\(_2\). Passive Ni hydroxides have previously been reported to exhibit significant interfacial resistance to electron transports.56,57 The \( Z_w \) values of 26.76 and 16.28 \( \Omega \cdot s^{-1/2} \) are recorded for Ni/MOFDC and AT-Ni/MOFDC, respectively. The values of “\( a \)” (i.e., 0.88 and 0.76) which are less than 1.0 for an ideal capacitor mean pseudocapacitive behavior. Hence, AT-Ni/MOFDC displays superior specific capacity, increased OH\(^-\) ion diffusion, and more electrochemical conductivity in the three-electrode system; subsequent investigations were performed only with the chemically etched material (AT-Ni/MOFDC). Moreover, AT-Ni/MOFDC possesses a higher capacity to charge storage, as evident from the values of its \( C_{\text{dl}} \) and CPE, compared to Ni/MOFDC.

The energy storage mechanism of any electrode material may be categorized as follows: (i) capacitive (i.e., EDLC process, non-faradic reactions), (ii) diffusion-controlled (faradic reactions), or (iii) mixed processes (non-faradic and faradic processes). Considering the controversy and misinterpretation of the energy storage mechanism of Ni-based electrodes, we thought that it is necessary to establish the process(es) that dominate(s) the AT-Ni/MOFDC electrode material. From the fundamental concepts of cyclic voltammetry (CV), the current response \( (i/A) \) relates to the scan rate \( (\nu/V \cdot s^{-1}) \) through the power law relationship (eqs 3 and 4)58–62

\[
i = a \cdot \nu^b
\]

\[
\log j = b \log \nu + \log a
\]

where \( j \) represents the current density, while \( a \) and \( b \) represent adjustable parameters that can easily be obtained from the plot of \( \log j \) against \( \log \nu \). A value of \( b = 1 \) means that the dominant energy storage mechanism is an adsorption-controlled, pure capacitive (i.e., non-faradic) process; a value of \( b = 0.5 \) means that the storage mechanism is a diffusion-controlled (i.e., faradic) process; and a value of \( b \) greater than 0.5 but less than 1.0 suggests a mixed mechanism (i.e., both faradic and non-faradic processes in operation). As shown in Figure 5a,b, the \( \log-\log \) plots show that the \( b \) values are greater than 0.5 (i.e., 0.56 and 0.61 for Ni/MOFDC and 0.59 and 0.77 for AT-Ni/MOFDC), indicating that both systems (Ni-rich and Ni-starved complexes) exhibit a mixed faradic-capacitive mechanism.

| EIS parameters | Ni/MOFDC | AT-Ni/MOFDC |
|---------------|---------|-------------|
| \( R_s/\Omega \) | 0.30 ± 0.01 | 0.30 ± 0.01 |
| \( R_{\text{int}}/\Omega \) | 26.81 ± 1.10 | 18.16 ± 1.00 |
| \( C_{\text{dl}}/\mu F \) | 4.75 ± 1.01 | 7.25 ± 1.23 |
| \( R_{\text{ct}}/\Omega \) | 100.20 ± 0.50 | 13.63 ± 0.09 |
| CPE/mF \cdot s\(^{1/2}\) | 6.66 ± 1.41 | 110.80 ± 11.99 |
| \( a \) | 0.88 | 0.76 |
| \( Z_w/\Omega \cdot s^{-1/2} \) | 29.76 ± 0.01 | 16.28 ± 0.01 |

Figure 5. (a) Log peak current versus log scan rate for Ni/MOF, (b) log peak current versus log scan rate for AT-Ni/MOF, (c) comparison of the capacitive and diffusion-controlled contributions fraction for AT-Ni/MOFDC at 5 mV s\(^{-1}\), and (d) histograms of the percentage contributions at 5–50 mV s\(^{-1}\).
From the same voltammetric concept, the power law equation can be separated into capacitive and faradic current responses in eqs 5 and 6, respectively:

- Capacitive (adsorption-controlled) current response:  
  \[ i \propto \nu, \Rightarrow i = k_1 \nu \]  
  (5)

- Faradaic (diffusion-controlled) current response:  
  \[ i \propto \nu^{1/2}, \Rightarrow i = k_2 \nu^{1/2} \]  
  (6)

Thus, the total current response at a given potential (V) can be as given in eqs 7 and 8

\[ i = k_1 \nu + k_2 \nu^{1/2} \]  
(7)

\[ i/\nu^{1/2} = k_1 \nu^{1/2} + k_2 \]  
(8)

where \( k_1 \) and \( k_2 \) are constants that describe the capacitive and faradic current contributions, respectively. Thus, by plotting \( i/\nu^{1/2} \) against \( \nu^{1/2} \), the values of \( k_1 \) and \( k_2 \) can be obtained. Thus, by calculating the \( k_1 \) value at different voltages and various scan rates, the capacitive current contributions can be plotted and differentiated from the faradic contributions, as exemplified in Figure 5c,d.

Figure 5c shows the typical voltage profile for the capacitive current in comparison with the total current at a scan rate of 5 mV s\(^{-1}\). From the histogram, comparing the percentage contributions of the faradic to non-faradic processes (Figure 5d), it is interesting to observe that battery-type storage (faradic process) dominates at low scan rates while EDLC-type storage (non-faradic process) dominates at high scan rates, indicating that the AT-Ni/MOFDC electrode material possesses unique characteristics of high energy and high power (rate capability). In general, the energy storage mechanism of the Ni-based battery-type electrode material, in contrast to literature, is a mixed faradic/capacitive process. The cycle stability of the Ni-based electrodes is shown in Supporting Information, Figure S5, which proves that the electrodes are stable after 2000 cycles.

### Full Cell Battery-Type Energy Storage (BTES) Device

The BTES device was fabricated with 3.0 M KOH electrolyte using the AT-Ni/MOFDC and acetylene black (AB) as the positive and negative electrodes, respectively. Figure 6a shows the potential windows of the AB and AT-Ni/MOFDC electrodes running at 50 mV s\(^{-1}\). Figure 6b shows the CV curves of the BTES device at different scan rates with a potential window of 1.6 V. Figure 6c shows typical charge–discharge cycling showing battery-type features, with the nominal voltage of 1.3 V. The device shows better charge–discharge features at higher current densities (\( \geq 0.75 \text{ mA g}^{-1} \)). Figure 6d compares the discharge capacity at different current densities (0.75–5 mA g\(^{-1}\)) with 25 mAh g\(^{-1}\) at 0.75 A g\(^{-1}\), showing 30% capacity retention even at a high rate, 5 A g\(^{-1}\).

Cycling stability is a crucial requirement for any electrochemical energy storage device. Figure 7a depicts the capacitive retention and Coulombic efficiency of the AT-Ni/MOFDC/AB device tested at 4 A g\(^{-1}\) in the voltage window of 0.0–1.6 V. After 2000 cycles, the AT-Ni/MOFDC/AB maintains capacity retention as high as 88% with a small capacity fading, indicating that the device exhibits good electrochemical cycling stability. In addition, the device maintained long-term electrochemical cycling (2000 cycles) with a high Coulombic efficiency of \( \sim 100\% \).

The morphological and structural changes in an electrochemical system such as the BTES studied in this work are best established by the changes that occur at the solid–solution interface (also known as the electrode–electrolyte interface, EEI). EIS is best used to understand the interfacial electrochemistry and explain cycling stability. Figure 7b compares the Nyquist plots obtained before and after 2000 cycles. The EIS parameters before and after 2000 cycles (modeled with the simple Randles electrical equivalent circuit, EEC, Figure 7b, inset) comprise (i) the bulk resistance (\( R_b \)) due to the combined resistances arising from the current collectors, electrodes, electrolyte, and separator; (ii) the charge-transfer resistance (\( R_{ct} \)) due to electron transport; (iii) the CPE due to the inhomogeneous or irregular structure or morphology of the
electrode surfaces; and (iv) $Z_w$ due to resistance to ionic diffusion, as previously explained. The modeled parameters are summarized in Table 3. The $R_b$ value remained essentially the same before and after cycling ($\sim 0.4 \Omega$), while the $R_{ct}$ value decreased slightly after the 2000th cycle (from $\sim 2.0$ to 1.6 $\Omega$), suggesting slight activation of the EEI layer leading to enhanced conductivity. The "$a$" values of the CPE increased from 0.72 (before cycling) to 0.79 (after the 2000th cycle), showing that the electrode material maintains its mixed mechanism of pseudocapacitance: it is neither a pure faradic process (where $a = 0.5$) nor a pure EDLC process (where $a = 1.0$). Finally, the $Z_w$ value increased by a factor of $\sim 2.5$ after the 2000th cycle, indicating a decreased ionic diffusion in the bulk AT-Ni/MOFDC//AB electrode material. In general, the EIS data prove that the structure of the EEI layer, where electrochemistry occurs, changed slightly upon long-term cycling, corroborating the satisfactory stability (capacity retention of $\sim 88\%$ after 2000 cycles), as shown in Figure 7a.

Also, changes in the EEI layer can be determined from the power capability of the BTES device before and after long-term cycling by analyzing the knee frequency ($f_0$/Hz):54 a high value of $f_0$ is an indication that the BTES possesses high power density. Prior to cycling, the BTES shows a higher $f_0$ value (ca. 877 Hz, response time, $\tau$, of 1.1 ms) than after the 2000th cycle (ca. 591 Hz, response time, $\tau$, of 1.7 ms). This slight change in the response times also confirms the stability of the EEI layer of the electrode materials. The phase angles of the AT-Ni/MOFDC//AB BTES before (40°) and after 2000 cycles (45°) are obtained from the Bode plots (Figure 7c,d) corroborating the diffusion process.

Figure 7e compares the specific energy versus specific power density (Ragone plot) of the BTES device studied in this work with some recent reports. The AT-Ni/MOFDC//AB device exhibits a high energy density (33 Wh kg$^{-1}$) and power density (983 W kg$^{-1}$). In addition, the energy and power densities are much higher than those of many asymmetrical supercapacitors (i.e., calculated with $F/g$) such as Ni(OH)$_2$/g-C$_3$N$_4$/AC (17.6 Wh kg$^{-1}$ and 130 W kg$^{-1}$),63 Ni(OH)$_2$/Ni-foam//AC (27.2 Wh kg$^{-1}$ and 240 W kg$^{-1}$),64 Ni(OH)$_2$/GR (30 Wh kg$^{-1}$ and 730 W kg$^{-1}$),65 and Ni(OH)$_2$/AC (32.9 Wh kg$^{-1}$ and 800 W kg$^{-1}$).56 Also, the specific capacity of AT-Ni/MOFDC is higher than

Table 3. EIS Parameters of AT-Ni/MOFDC//AB BTES Device Before and After the 2000th Cycle

| EIS parameters | AT-Ni/MOFDC//AB BTES device before 2000 cycles | AT-Ni/MOFDC//AB BTES device after 2000 cycles |
|----------------|-----------------------------------------------|-----------------------------------------------|
| $R_b$/$\Omega$ | 0.38 ± 0.340                                  | 0.40 ± 1.61                                  |
| $R_{ct}$/$\Omega$ | 2.01 ± 0.12                                 | 1.59 ± 0.16                                  |
| CPE/mF$\cdot$s$^{(a-1)}$ | 0.30 ± 0.03                               | 1.19 ± 0.09                                  |
| $a$ | 0.72                                         | 0.79                                         |
| $Z_w$/S$^{-1/2}$ | 10.07 ± 0.52                                | 26.03 ± 0.85                                 |
| $f_0$/Hz | 876.96                                      | 590.95                                       |
| $\tau$/ms | 1.14                                        | 1.69                                         |
| phase angle | 40°                                          | 45°                                           |

Figure 7. Electrochemical performance of the AT-Ni/MOFDC//AB BTES device: (a) typical cycling performance at 4 A g$^{-1}$, (b) Nyquist plots obtained before and after 2000 charge–discharge cycles, (c, d) Bode plots before and after 2000 cycles of the AT-Ni/MOFDC//AB BTES, (e) comparative Ragone plot of this work with recent literature, and (f) optical image of 1.6 V red light emitting diode (LED) bulb lit up by the device.
that previously reported for NCMS/rGO. To demonstrate the practical application of the device, a 1.6 V red LED was easily powered and lasted for about 6 min after charging to 3.2 V for 30 s, as shown in Figure 7f.

■ CONCLUSIONS

Ni-MOF has been successfully synthesized via microwave-assisted solvothermal synthesis and explored as a sacrificial template to prepare the Ni/MOFDC composite and subsequently etched with acid, yielding AT-Ni/MOFDC that gives different physicochemical properties such as well-dispersed metallic Ni nanoparticles on the MOFDC, removal of the passive Ni(OH)₂, increased surface area, induced oxygen vacancy, and defect. These new properties of AT-Ni/MOFDC are beneficial for the energy storage applications compared to the untreated sample (Ni/MOFDC). AT-Ni/MOFDC displays superior electrochemical properties for battery-type energy storage in terms of lower series resistance, increased specific capacity, among others in the three-electrodes system, relative to the untreated analog (Ni/MOFDC). It is proven that the energy-storage mechanism of this novel Ni-based electrode material is controlled by the faradic and non-faradic processes, depending on the scan rate. The assembled AT-Ni/MOFDC//AB BTES device exhibits a high specific capacity of 25 mAh g⁻¹ at a current density of 0.75 A g⁻¹. Additionally, the device has a high energy density of 33 Wh kg⁻¹ and a power density of 983 W kg⁻¹ compared to recent literature, and excellent cycling performance with ≈88% capacity retention after the 2000th cycle. This study opens up a new route to explore the MOF sacrificial template for making electrode materials with mesoporous carbon support for the development of high-performance BTES.

■ EXPERIMENTAL SECTION

Materials. All chemicals and solvents were used as received with no further purifications. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%), trimeric acid (TMA, C₉H₆O₆, 99.9%), triethylamine (TEA, N(CH₂CH₃)₃, 99.5%), and ethylene glycol (EG, C₂H₆O₂, 99.8%) were purchased from Sigma-Aldrich. Ethanol (C₂H₆O, 99%), quartz boat, quartz tube, and pure nitrogen (N₂) were supplied by Afrox (South Africa). Millipore water (resistivity value of 18.2 MΩ cm collected from the Milli-Q water system), hydrochloric acid (HCl), potassium hydroxide (KOH, 85 %), carbon paper and nickel foam were also used.

Preparation of Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC. A nickel-based metal–organic framework (Ni-MOF) was synthesized using a microwave-assisted solvothermal strategy, schematically shown in Figure 8.

Briefly, 1.1632 g (4.0 mmol) of Ni(NO₃)₂·6H₂O, 1.6811 g (8.0 mmol) of TMA, and 10 mL (1.2 mol) of TEA were dissolved in 50 mL (0.9 mol) of EG in a flask. The mixture was ultrasonicated for 1 h to attain uniformity. Then, the mixture was subjected to microwave (MW) irradiation at 600 W and 150 °C for 30 min and cooled to room temperature. A deep green crystal of the Ni-MOF was obtained, washed three times with ethanol by centrifugation to remove any impurities, and then dried in a vacuum oven at 80 °C for 12 h. The synthesized Ni-MOF powder was poured in a quartz boat, placed in a quartz tube, and annealed in an electric furnace from 25 to 900 °C in N₂ flow at the rate of 5 °C min⁻¹ for 3 h and then maintained at 900 °C for an additional 1 h, resulting in nickel-nanoparticle-supported MOF-derived carbon (Ni/MOFDC). The as-prepared Ni/MOFDC was divided into two portions: one portion was chemically etched with 3.0 M HCl (10 mL), giving AT-Ni/MOFDC, while the other portion was left untreated (i.e., Ni/MOFDC).

Characterization of Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC. The materials were thoroughly characterized using Fourier transform infrared spectroscopy (FTIR, BRUKER TENSOR 27), Raman spectroscopy (BRUKER SENTERRA), powder X-ray diffraction (XRD, BRUKER D2 diffractometer equipped with Cu Kα radiation (λ = 1.54178 Å)), X-ray photoelectron spectroscopy (AXIS SUPRA XPS equipped with an Al Kα radiation source (1486.6 eV)), transmission electron microscopy (FEI Tecnai T12 Sprint TEM), scanning electron microscopy (FEI Nova Nanolab 600 SEM), coupled with energy-dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET, Micrometric Tristar 3000) to determine the presence of functional groups, bond vibrations, crystalline structures, chemical environments, morphological properties, surface area, and pore sizes, respectively.

Electrochemical Measurements. Fabrication and Electrochemical Study with a Three-Electrode System. Electrochemical measurements were performed with the three-electrode system, connected to a Bio-Logic SP300 electrochemical workstation running on EC-Lab software. The Ni/MOFDC and AT-Ni/MOFDC active materials were separately dispersed in ethanol and stirred for 2 h to form two different slurries. Then, each slurry was coated onto a carbon paper
current collector as the working electrode, followed by drying in a vacuum oven overnight. The mass loadings were between 1.5 and 1.7 mg for all electrodes. A Ni-based material (i.e., Ni/MOFDC and AT-Ni/MOFDC) coated on the carbon paper served as the working electrode, Ni foam served as the counter electrode, silver wire as the reference electrode, while a 3.0 M KOH solution served as the electrolyte. Cyclic voltammetry (CV), galvanostatic charge—discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the energy storage capability of the materials. The EIS experiments were performed under an AC voltage of 10 mV amplitude in the frequency range from 0.1 Hz to 100 kHz.

Fabrication and Electrochemical Study of the Battery-Type Energy Storage (BTES) System (AT-Ni/MOFDC//Acetylene Black (AB)). The assembly of the BTES was carried out with AT-Ni/MOFDC as a cathode while acetylene black (AB) as an anode, with 3.0 M KOH as the electrolyte. For charge balancing, the mass ratio of the cathode material to the anode material (obtained from three-electrode experiments) was determined using the conventional methods (eqs 9 and 10).

\[ q^+ = q^- \]  
\[ m^+ \times \frac{c^+}{c^-} = \Delta V^- \times \frac{\Delta V^+}{\Delta V^-} \]  

where \( q^+ \) and \( q^- \) are the charges at the cathode and anode, respectively. The optimal mass ratio was obtained using eq 10.

\[ \frac{m^+}{m^-} = \frac{c^+}{c^-} + \frac{\Delta V^-}{\Delta V^+} \]  

where \( m^+ \), \( \Delta V^+ \), and \( c^+ \) are the mass, potential window, and specific capacity of the cathode, respectively, while \( m^- \), \( \Delta V^- \), and \( c^- \) are the mass, potential window, and specific capacity of the anode, respectively. Voltammetric specific capacity (\( C_s \)), power density (\( P_p \)), and energy density (\( E_s \)) are following eqs 11 and 12.

\[ C_s = \frac{\int I dV}{3.6 \text{ mS}} \text{ (mAh g}^{-1} \text{)} \]  
\[ C_s = \frac{I \times \Delta t}{3.6 \text{ m}} \text{ (mAh g}^{-1} \text{)} \]  

where \( I dV \text{ (A-V)} \) is the voltammetric charge, which is an area under the curve of the CV. S(V s\(^{-1}\)) is the scan rate, I(A) is the discharging current, \( \Delta t \) is the discharge time, and \( m \text{ (g)} \) represents the active mass of the electrodes.

Specific energy (\( E_s \text{ Wh kg}^{-1} \)) and specific power (\( P_p \text{ W kg}^{-1} \)) are calculated from the discharge curves using the conventional formulae (eqs 13 and 14) for the battery and battery-type energy storage.

\[ E_s = \frac{I \times V \times \Delta t}{m} \text{ (Wh kg}^{-1} \text{)} \]  
\[ P_p = \frac{E_s}{\Delta t} \text{ (W kg}^{-1} \text{)} \]

where \( E_s \text{ (Wh kg}^{-1} \) represents the specific energy, \( I \text{ (A)} \) defines the discharging current, \( V \text{ (V)} \) is the voltage, \( m \text{ (kg)} \) is the total mass of the two electrode materials, \( P_p \text{ (W kg}^{-1} \) is the specific power, and \( t \text{ (h)} \) is the time of discharge.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02563.

FTIR results of Ni-MOF, Ni/MOFDC, and AT-Ni/MOFDC; TEM micrograph of Ni-MOF; SEM images of the Ni/MOFDC and AT-Ni/MOFDC; and EDX spectra of Ni/MOFDC and AT-Ni/MOFDC; Table S1 for Raman curve-fitting data, CV and GCD curves of Ni/MOFDC and AT-Ni/MOFDC at different scan rates and current densities, cycling performance of the electrodes, and GCD curves of AT-Ni/MOFDC//AB at different current densities (PDF)

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T.P.M. and A.K.I. made equal contributions to this work.

**Notes**

The authors declare no competing financial interest.

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