Nickel-based pillared MOFs for high-performance supercapacitors: design, synthesis and stability study

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Abstract: We have successfully synthesized novel, nickel-based, pillared DABCO-MOFs (DMOFs) of similar topologies--- $[\text{Ni}(\text{L})(\text{DABCO})_{0.5}]$, where L is the functionalized BDC (1,4-benzenedicarboxylic acid) linker and DABCO is 1,4-diazabicyclo[2.2.2]-octane. The stability of DMOF-ADC ($[\text{Ni}(9,10\text{-anthracenedicarboxylic acid})(\text{DABCO})_{0.5}]$) and DMOF-TM ($[\text{Ni}(2,3,5,6\text{-tetramethyl-1,4-benzenedicarboxylic acid})(\text{DABCO})_{0.5}]$) in a humid environment was confirmed by surface area analysis on the water-exposed samples. When used as electrode materials, these DMOF capacitors exhibited excellent electrochemical performance. For example, a Ni-DMOF-ADC electrode showed specific capacitances of 552 and 438 F g^{-1} at current densities of 1 and 20 A g^{-1} , respectively, while maintaining outstanding cycling stability (capacitance retention of >98% after 16,000 cycles at current density of 10 A g^{-1}) for MOF-derived materials based supercapacitors. The excellent electrochemical performance is attributed to the conversion of DMOFs to highly functionalized nickel hydroxide which inherited the high stability of DMOF-ADC and remained intact during charge-discharge process. Further, this work provides a general approach for the application of nickel-based pillared MOFs as relatively stable electrode in electrical energy storage.

Key words: Ni-DMOF; ligand selection; highly functionalized nickel hydroxide; supercapacitor; long cycle life

Introduction

Supercapacitors (SCs) have attracted increasing attention as novel energy storage devices due to their higher power densities, faster charge-discharge rates, and longer cycling lives than conventional rechargeable batteries [1-3]. According to the physicochemical processes responsible for energy storage, SCs are generally classified into (i) electrical double layer capacitors (EDLCs) where the energy storage is associated with charge separation within double layers (e.g. porous carbon materials [4, 5]) and (ii) pseudocapacitors which utilize near-surface redox reactions of transition metal oxides and hydroxides materials [6-8]. In general, EDLCs offer a very high charge/discharge rate with a long cycle life but have low capacitance, while pseudocapacitors have high capacitance but slightly inferior rate capability and cycling life [4-8].

To narrow the performance gap between these two types of capacitors, rational design of advanced electrode materials is necessary. Metal organic frameworks (MOFs) are drawing much attention as a potential electrode candidate for SCs [9-17] due to their remarkable surface areas, facile tunable pore size, and peculiar structures with potential pseudo-capacitive redox centers [17] either utilized as porous metal oxides [9, 10], porous carbon templates [11-13] or in a direct application as a new type of electrode material [14-16]. However, the instability of most MOFs or MOF-derived electrode material during charge-discharge process is widely considered a major limitation for their application in SCs [18].

To achieve an improved cycling performance, we tried to synthesize kinetically stable MOFs via ligand functionalization. Our previous work demonstrates that it is possible to adjust the

water stability of pillared MOFs both in the positive and negative directions by proper functionalization of the BDC ligand [19-21]. Notably, placing nonpolar groups (e.g., -methyl) on the BDC linker leads to enhanced stability of DMOF, while placing polar groups (e.g., -OH) on the BDC linker has no such effect on the structure compared to the original one. Besides, Tan et al. [22] also found the stability of different metal based isostructural DMOFs $[M(\text{BDC})(\text{DABCO})_{0.5}]$ follows the order of $\text{Cu-DMOF} < \text{Ni-DMOF} > \text{Zn-DMOF} > \text{Co-DMOF}$ which corresponds to the bond dissociation energy of diatomic molecules metal-oxygen and overall formation(stability) constants of metal amine complexes.

Herein, we summarized previous results [19-22] and synthesized nickel-based, pillared MOFs of similar topology using 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid (TM), 1,4-naphthalenedicarboxylic acid (NDC) and 9,10-anthracenedicarboxylic acid (ADC) as carboxylate ligands and 1,4-diazabicyclo[2.2.2]octane (DABCO) as pillar ligands and have successfully confirmed the water stability of Ni-DMOF-ADC and Ni-DMOF-TM. When used as electrodes for SCs, the Ni-DMOF-ADC derived highly functionalized nickel hydroxide electrode inherited the high stability of DMOF-ADC and showed excellent cycling performance, the capacitance retention after 16000 cycles at 10 A g^{-1} was $>98\%$, which was much higher than that of the relatively less stable Ni-DMOF-TM and the unstable Ni-DMOF-NDC derived electrodes. These results indicate the impact of DMOFs' structure stability on long-term cycling stability and show that water stable DMOFs could be a promising electrode material for long cycle-life electrochemical capacitors.

Experimental section

Synthesis of DMOF: The Ni-DMOF-ADC was synthesized by using a simple solvothermal method modified from literature [23]. All the chemicals were commercially available and used as obtained without further purification. Typically, 1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 mmol of ADC, and 0.5 mmol of DABCO were dissolved in 10 mL of DMF at room temperature in a glass beaker and the resulting slurry was stirred for 2h . After filtering the solution, the filtrate was poured into a Teflon-lined stainless steel reactor and kept in a preheated oven at 120 °C for 2 days. The resulting materials were filtered and washed with DMF repeatedly after cooling to room temperature in air. Ni-DMOF-TM was synthesized according to the work of Jasuja et al. [18] and Ni-DMOF-1,4-NDC (Ni-DMOF-NDC) was firstly prepared with slight modification from the literature [22] for Zn-DMOF-1,4-NDC; i.e., by dissolving 0.63 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.63 mmol of 1,4-NDC, and 0.31 mmol of DABCO in 15 mL of DMF in a glass beaker and kept stirring for 2 h at room temperature. The rest of the procedure was the same as that of Ni-DMOF-ADC. All the activated samples could be prepared by heating at 110 °C for 12 h under dynamic vacuum condition.

Characterization: The crystallographic structures of the materials were obtained using an X'Pert X-ray PANalytical diffractometer with an X'celerator module and $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature, with a step size of 0.02° in 2θ . The nitrogen isotherms of the materials were measured at 77K using a Quadrasorb system from Quantachrome Instruments. Applying the Brunauer–Emmett–Teller (BET) model to these isotherms, specific surface areas were determined for each material. Raman spectroscopy was used for the structural analyses on both fresh and cycled electrode materials. FTIR was used to determine different functional groups in electrode materials. The microstructure and morphology were examined by using a scanning electron microscope (Zeiss Ultra60 FE-SEM).

Water vapor adsorption isotherms were collected at 22 °C and 1 bar using a 3Flex Surface Characterization Analyzer from Micromeritics. The samples (~30-40 mg) were activated in situ (110 °C, under dynamic vacuum) to evacuate any guest molecules from the framework prior to water vapor adsorption measurements. Experiments were conducted only up to $P/P_0=0.90$ to ensure water condensation did not occur in the instrument. After dosing, each adsorption and desorption point was checked every 5 seconds to evaluate whether equilibrium had been reached within a 0.01% tolerance.

Electrochemical measurement: Cyclic voltammetry (CV) and galvanostatic charge-discharge tests were carried out using a classic three-electrode configuration. For the working electrode, a mixture containing of 70 wt% active material, 20 wt% Super P Li, and 10 wt% PTFE binder was well mixed then rolled with the assistance of ethanol to form a uniform film with a typical areal mass of approximately 1.9 mg cm^{-2} . The film electrode was then pressed between two nickel foam, and dried under vacuum at 80 °C for 12 h. A platinum mesh electrode and an Ag-AgCl electrode prefilled with 4 M KOH aqueous solution saturated with AgCl were used as the counter and the reference electrodes, respectively. The cyclic voltammograms were acquired in a potential range between 0 and 0.5 V at different scan rates, and the charge-discharge processes were performed by cycling the potential from 0 to 0.45 V at different current densities in a 2 M KOH aqueous electrolyte. To avoid capacitance from Ni foam during the cycling process [26], we fabricated an asymmetric capacitor with a Ni-DMOF-based anode and an AC-based cathode. The cyclic stability was evaluated by galvanostatic charge-discharge measurements at a current density of 10 A g^{-1} . All the nickel-based, pillared DMOF used for high performance SC electrochemical measurements were conducted using a Solartron SI 1286 electrochemical workstation.

Result and Discussion

Characteristics of Ni-DMOFs

The crystallinity and purity of the prepared DMOF samples was confirmed by comparing with simulated patterns from single crystal X-ray diffraction (**Fig. S1**, Supporting Information). Similarities among all the patterns were evident; these frameworks are isostructural to the simulated pattern, suggesting that all the MOFs probably had a layered topology (CCDC no. 992483) which can be described as metal paddle-wheel clusters connected by functionalized BDC ligands to form 2-D layers that are further pillared together by DABCO ligands to 3-D structure (**Fig. 1**) [23]. N₂ adsorption-desorption isotherms (**Fig. S2**, Supporting Information) at 77 K on the activated MOF samples showed typical type I behavior according to the IUPAC classification [24].

Fig 1. (a) Schematic illustration of the synthesis process of DMOFs and wireframe view of 3D Ni-DMOF-ADC along (b) the (1, 0, 0) surface and (c) the (0, 0, 1) surface. Blue: nitrogen; Green: nickel; Grey: carbon and H atoms are omitted for clarity.

Structural Stability Analysis under Humid Environments

To investigate the water stability of examined structures, several detailed characterization methods were performed on each nickel-based DMOF variation, including water vapor adsorption isotherms, PXRD patterns, SEM and surface area from BET modeling [25] of N₂ adsorption isotherms before and after water exposure. **Figure 2(d)** shows the water vapor adsorption-desorption isotherms at 22 °C for Ni-DMOF-ADC, Ni-DMOF-TM, and Ni-DMOF-NDC. The water vapor adsorption capacities observed at P/P₀=0.9 are 16.78 mmol/g for Ni-DMOF-ADC, 25.10 mmol/g for Ni-DMOF-TM, and 15.34 mmol/g for Ni-DMOF-NDC. The type V isotherm profiles of the examined samples is likely a result of the presence of nonpolar groups (-methyl, -naphthalene, and -anthracene) within the porous structure [19]. In agreement with the trend found in literature [18], Ni-DMOF-ADC and Ni-DMOF-TM show non-negligible hysteresis loops, indicating some amount of water is retained in the pores and cannot be fully desorbed, even using dry air as the stream (0% RH point in the desorption isotherm). Various levels of flexibility [26] or defects [24] may play an important role in this phenomenon. Ni-DMOF-NDC retains 42% of maximum uptake which is much higher than 18% for Ni-DMOF-ADC and 9% for Ni-DMOF-TM, suggesting Ni-DMOF-NDC is degraded upon water exposure. Indeed, Ni-DMOF-NDC sample was significantly degraded upon water vapor exposure, as shown in SEM images before and after water exposure **Figure 3(c, f)**. In addition, Ni-DMOF-NDC displayed significant change in crystallinity and loss of surface area **Table 1** after water exposure. This result is consistent with the work reported by Jasuja et al. [20], demonstrating that zinc-based DMOF-1,4 NDC was not stable upon water exposure.

Fig 2. XRD patterns of as-synthesized and water exposed (after 90% RH) (a) DMOF-ADC, (b) DMOF-TM, (c) DMOF-NDC, (d) Water vapor adsorption isotherms at 22 °C for desolvated compounds of DMOF-functionalized BDC (closed symbols means adsorption; open symbols means desorption) Lines connecting the points are to facilitate viewing.

On the other hand, no obvious change in PXRD patterns (**Figure 2(a), 2(b)**) or loss of surface area (**Table 1**) was observed in both Ni-DMOF-ADC and Ni-DMOF-TM samples after water exposure, illustrating Ni-DMOF-ADC and Ni-DMOF-TM retain their porous structures after adsorbing large amounts of water (>15 mmol/g at 90% relatively humidity (RH)). In addition, almost no change in either crystal size or morphology was observed from SEM images of Ni-DMOF-ADC (**Figure 3(a, d)**) and Ni-DMOF-TM (**Figure 3(b, e)**) before and after water

exposure. The stability of Ni-DMOF-ADC and Ni-DMOF-TM could be attributed to the presence of nonpolar groups on the BDC linker.

Table 2. Comparison of properties of nickel-based pillared MOFs synthesized in this work.

MOF	Activation Process (under dynamic vacuum)	Features	Total Pore Volume ^a (cm ³ /g)	BET Surface Area (m ² /g)	BET Surface Area (after 90% RH)	Stability
Ni-DMOF-NDC	110 °C (12h)	Noncatenated	0.428	943	0.78	Unstable
Ni-DMOF-TM	110 °C (12h)	Noncatenated	0.453	1036	960	Stable
Ni-DMOF-ADC	110 °C (12h)	Noncatenated	0.365	783	760	Stable

^aCalculated from N₂ adsorption at 77 K at P/P₀ = 0.8.

Fig 3. FESEM images of (a) Ni-DMOF-ADC, (b) Ni-DMOF-TM, (c) Ni-DMOF-NDC before water adsorption experiments, and (d) Ni-DMOF-ADC, (e) Ni-DMOF-TM, (e) Ni-DMOF-NDC after water adsorption experiments.

Electrochemical Properties

The structural stability analysis revealed that Ni-DMOF-ADC and Ni-DMOF-TM had a large surface area which can be fully preserved under 90% RH, making them an ideal choice for materials applied in positive electrodes of supercapacitors. Ni-DMOFs were investigated as a three-electrode configuration and the results are shown in **Fig. 4(a)** to **Fig. 4(d)**. Cyclic voltammetric (CV) curves of Ni-DMOF-TM, Ni-DMOF-ADC and Ni-DMOF-NDC electrodes at a scan rate 10 mV s^{-1} were shown for comparison in **Fig. 4(a)**. For all the DMOFs, a pair of well-defined redox peaks within 0.15-0.45 V were observable, indicating typical pseudocapacitive behavior. The specific capacitances are correlated to the average area of a CV curve which follow the order of Ni-DMOF-ADC > Ni-DMOF-TM > Ni-DMOF-NDC.

Fig 4. Electrochemical performance of the Ni-DMOF electrode. (a) Cyclic voltammograms for Ni-DMOF-ADC, Ni-DMOF-TM and Ni-DMOF-NDC at a scan rate of 10 mV s^{-1} in 2M KOH. (b)

Galvanostatic charge/discharge curves of Ni-DMOF-ADC at different constant current densities. (c) CV curves of Ni-DMOF-ADC at scan rates 10, 30 and 50 mV s⁻¹. (d) Specific capacitance of Ni-DMOF-ADC as a function of the current densities calculated from the corresponding discharge curve for each current density.

Fig. 4(c) shows the CV response of Ni-DMOF-ADC at different scan rates ranging from 10 to 30 mV s⁻¹. With increasing scan rate, the current response increased accordingly, indicating the good rate property. Charge-discharge curves of Ni-DMOF-ADC **Fig. 4(b)**, Ni-DMOF-TM and Ni-DMOF-NDC (**Fig. S3**, Supporting Information) at various current densities in a potential range of 0-0.45V were collected which further confirmed the CV analysis. The discharge curves of the samples at the current density of 1 A g⁻¹ show a significant deviation from a straight and flat line, indicating the capacitance results primarily from pseudocapacitive behavior. The specific capacitance could also be calculated from the galvanostatic charge-discharge measurements using the following equation [27]:

$$C = \frac{2i_m \int V dt}{V^2 \Big|_{V_i}^{V_f}} \quad (1)$$

C represents the galvanostatic charge-discharge (GCD) specific capacitance. $\int V dt$ is the integral current area, where V is the potential with initial and final values of V_i and V_f , respectively. $i_m = I/m$ is the current density, where I is the current and m is the active mass of the electrode. The calculated specific capacitance as a function of the discharge current density was plotted in **Fig. 4(d)**. The specific capacitances were in the order of Ni-DMOF-ADC > Ni-DMOF-TM > Ni-DMOF-NDC. The specific capacitances of Ni-DMOF-ADC negatively correlated with current density and were calculated to be 552 F/g and 395 F/g at 1 A/g and 50 A/g, which are very close to theory estimation, implying efficient utilization of the MOF structure during charge-discharge measurement. With an increase of current density to 50 A/g, the specific capacitance retained

71.6%, 68.1% and 50.4% compared to their initial values of 1 A/g for Ni-DMOF-ADC, Ni-DMOF-TM and Ni-DMOF-NDC, respectively, indicating better ion diffusion and electron transportability for more stable DMOFs at high current density.

The cycling stability is the most important factor for electrochemical capacitors in practical applications. It has been reported that with increasing cycle number, nickel foam as the current collector for three electrode system in alkaline electrolyte will contribute to the capacitance during the charge-discharge process which leads to non-ignorable error to the results [28]. So we fabricated an asymmetric capacitor with a Ni-DMOF-based anode and an AC-based cathode to evaluate cyclic stability, in which nickel foam was no longer used. The CV curves obtained for the AC electrode are shown in the (**Fig. S4**, Supporting Information) and the calculated specific capacitance was 206 F g⁻¹ at a scan rate of 10 mV s⁻¹. As for asymmetric supercapacitors, the charge balance between the two electrodes needs to follow the relationship $q^+ = q^-$, where the charge stored by each electrode usually depends on the specific capacitance (C), the potential range for the charge/discharge process (ΔE), and the mass of the electrode (m) following equation [29]:

$$q = C \times \Delta E \times m \quad (2)$$

in order to obtain $q^+ = q^-$, the mass balancing will be expressed as follows [29]:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+} \quad (3)$$

According to Equation (2), (3) and above analysis of the specific capacitance values and potential ranges for DMOF and AC, the mass ratio between the negative and positive electrodes (ADC, TM and NDC) of the asymmetric capacitor is 3.75, 3.16 and 1.95, respectively.

Electrochemical characterizations of the Ni-DMOF-based asymmetric supercapacitor demonstrated in **Fig. S5**. **Fig. 5** shows the cycling stability of the asymmetric supercapacitors for Ni-DMOF-ADC, Ni-DMOF-TM and Ni-DMOF-NDC in a potential range of 0-1.5 V at a current density of 10 A g^{-1} . After 16000 cycles, only 2% of the capacitance of DMOF-ADC-AC-based asymmetric supercapacitor was lost at this high current density, and the less stable TM one descended to 60% of its initial value after 9000 cycles while the unstable NDC asymmetric supercapacitor took only 2200 cycles to drop to 50%. Indicating the significant impact of DMOFs' structure stability on long-term cycling stability of related supercapacitors.

Fig 5. Cycle performance for all Ni-DMOFs-based asymmetric supercapacitor at a current density of 10 A g^{-1} .

In order to investigate the functioned material that contributed to the pseudocapacitive charge storage of the DMOF based capacitor, we performed experiments and analyses including SEM, Raman, FTIR and X-ray analyses to study the DMOF derived material. From XRD pattern (**Fig. 6(a)**), all of the diffractions are basically consistent with the pattern reported for nickel hydroxide [30], which matches well with the standard pattern (JCPDS 22-752). Raman spectroscopy was

used for the structural analyses on both fresh (**Fig. S6** supporting information) and cycled DMOF-ADC electrode material (**Fig. 6(b)**). After the DMOF-ADC electrode material cycled in 2 M KOH electrolyte, all of the Raman bands of the as-prepared Ni-DMOF disappeared. Instead, the cycled Ni-DMOF-ADC presented same Raman band characteristics with much reduced intensity, which includes a broad hump band within 400-650 cm^{-1} , which is the overlap of Ni-O stretching vibrations due to the complicated structure and a sharp band at 1055 cm^{-1} which correspond to CO_3^{2-} species. These band features suggest the DMOF-ADC derived material is not simple nickel hydroxide as reported by other works but turbostratic nickel hydroxide highly functionalized with carbonate ions most likely stored in the interlayer spacing. The significant difference between the fresh Ni-DMOF-ADC and cycled Ni-DMOF-ADC indicates the rather weak Ni-ligand coordination bond will be broken during electrochemical charge storage and will be replaced by stronger Ni-OH ionic/covalent bond. Also the carboxyl group bonded on anthracene ring will be oxidized, forming carbonate ions incorporated between the turbostratic $\text{Ni}(\text{OH})_2$ layers. Furthermore, the FTIR results suggested the highly functionalized nature of DMOF-ADC, the broad absorption band at around 3640 cm^{-1} could be assigned to the O-H stretching vibrations, which is the characteristic of $\text{Ni}(\text{OH})_2$ [31]. The peak around 1600-1640 cm^{-1} indicates the presence of C=O asymmetric stretching and $\delta\text{H}_2\text{O}$ vibration of the water molecule, and the band at 1380 cm^{-1} contributed by CO_3^{2-} anions further corroborate the fact that the presence of carbonate ions within the converted $\text{Ni}(\text{OH})_2$ structure. (**Fig. 6(c)**) [31, 32]. From SEM image (**Fig. 6(d) and Fig. 6(e)**), the microstructure of DMOF-ADC showed a micron-sized rod-like morphology, while the DMOF-ADC derived material inherited the external morphology from the MOF but with an obvious volume shrinkage of the nanorod. This

can be attributed to the substitution effect of the ADC and DABCO ligand to OH^- units at the presence of KOH.

Fig 6. (a)XRD pattern of DMOF-ADC converted material. (b) Raman spectra of DMOF-ADC electrode from 5000th, 10000th, 15000th cycle. (c) FTIR of DMOF-ADC converted material. FESEM images of (d) DMOF-ADC and (e) DMOF-ADC converted material.

The water stable DMOF-ADC derived structure converted to nickel hydroxide with incorporation of carbonate ions within its interlayer spacing in alkali, which remained stable during charge-discharge processes. The reason for the higher cycling stability of DMOF-ADC converted $\text{Ni}(\text{OH})_2$ based material were analyzed. First, the layered structure has a three-dimensional nanostructure inherited from MOFs, which provided a larger surface area (**Fig. S7** Supporting Information) compared to other nickel hydroxide, thus increasing the electrode-electrolyte contact area and decreasing the polarization of the electrode in charge-discharge cycles. Secondly, the low-crystalline nature of the structure is another factor for the high

stability. According to Li et al. [33], in supercapacitor tests, amorphous-phase or low-crystalline materials always have the potential to exhibit higher electrochemical performance and a longer cycle numbers than the materials with higher crystallinity because of its high structural disorder.

The strong Faradaic redox peaks may come from intercalation and deintercalation of OH^- during electrochemical reaction, which leads to reversible valence state changes between Ni^{2+} and Ni^{3+} . Overall, the detailed mechanism of the structure change and the final structure of MOFs after the charge/discharge processes were still not very clear yet, and further more advanced characterization methods are required.

MOFs were indicated to be very promising as electrode materials for supercapacitor applications due to their large surface area. However, one of the key problems remain to be solved before extensive application is how to keep original morphology and porous structure after calcination [34]. In order to overcome the structure collapse for most porous MOFs or MOF-derived materials, we synthesized novel water-stable pillared Ni-DMOF-ADC with good stability heritage and directly applied it as a supercapacitor electrode without morphology modification. Although Ni-DMOF-ADC converted to highly functionalized nickel hydroxide at the presence of alkali, the DMOF-ADC-derived supercapacitor's capacitance loss after 16000 cycles was only 2%. The excellent cycling stability of DMOF-ADC derived highly functionalized nickel hydroxide based capacitor is attributed to the high structure stability of the converted material inherited from DMOF-ADC structure. The cycling results reported in this paper is also superior to that of Ni-based electrode materials in other literatures [33, 35-39] (**Table S1** Supporting Information). The stability of functioned active material during charge-discharge process was also proved by XRD (**Fig. S8** Supporting Information) and Raman data (Fig, 5(b)).

Conclusions

In summary, we have synthesized novel isostructural nickel-based, pillared MOFs with different kinetic water stability based on our previous systematic study and applied them to supercapacitor electrode. Our study shows that the electrode made from the most stable Ni-DMOF-ADC had better electrochemical results in terms of specific capability and rate performance than the other two, and exceptional cyclic stability (98% after 16000 cycles) compared to other electrochemical studies based on MOFs or MOFs-derived materials. The excellent cycling stability of DMOF-ADC derived material based capacitor is attributed to the high structure stability of the converted highly functionalized nickel hydroxide inherited from DMOF-ADC. After all, we shed light on the important positive correlation between Ni-DMOFs structure stability and the electrochemical performance especially the cycling stability when directly used as electrode material of pseudocapacitor. This work opens new channel for the application of water stable metal-organic frameworks in energy storage.

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Graphical Abstract

TOC:

Biosketch:

Chong Qu

Chong Qu is currently a Ph.D. candidate under supervision of Prof. Ruqiang Zou, Peking University. He received his bachelor degree from School of Chemistry and Chemical Engineering at Nanjing University in 2013. He joined Prof. Meilin Liu's group as a GT-PKU joint program student at School of Materials Science and Engineering, Georgia Institute of Technology in 2014. His research interests include electrochemical materials based on crystalline porous frameworks for supercapacitors and Li-ion battery.

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Yang Jiao was born and raised in Tianjin, China. In 2012, he received his bachelor degree in Chemical Engineering from Tianjin University, China. He is currently a Ph.D. candidate in Professor Krista Walton's research laboratory at the Georgia Institute of Technology. His current research focus is to understand and enhance the performance of metal-organic frameworks in acid gas environments and experimental synthesis and design of nanoporous materials for supercapacitors and Li-ion battery applications.

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Bote Zhao is currently a post-doctoral fellow at the School of Materials Science and Engineering at Georgia Institute of Technology, USA. He received his B.S. and Ph.D. from Nanjing Tech University, China. His research experiences include work with binder-free films, nanostructured materials and graphene based materials for lithium-ion batteries and supercapacitors as well as the electrospinning synthesis of fibers, fabrication and water management of proton exchange membrane fuel cells, and hydrogen production from hydrous hydrazine.

He is currently focusing on the synthesis and characterization of novel materials for batteries, fuel cells, and supercapacitors.

Dongchang Chen

Dongchang Chen received his bachelor degree from department of chemical physics at University of Science and Technology of China in 2011. He is currently a Ph.D. candidate under supervision of Prof. Meilin Liu at School of Materials Science and Engineering, Georgia Institute of Technology. His research interests mainly focus on insitu spectroscopic study of solution-based electrochemical reactions.

Ruqiang Zou

Ruqiang Zou is currently the Professor of Materials Science and Engineering at the College of Engineering, Peking University. He received his PhD from Kobe University and the National Institute of Advanced Industrial Science and Technology (AIST), Japan under the supervision of Professor Qiang Xu. His

research interests focus on the controllable preparation of nanoporous materials for green energy utilization. He proposed a new strategy to construct hierarchically porous materials for single molecule adsorption, and extended their potential applications in hydrogen storage, carbon capture, and energy storage materials.

Krista S. Walton

Krista Walton was born in Florence, Alabama, and grew up in nearby Elgin. She received a B.S.E. degree from the University of Alabama—Huntsville and Ph.D. from Vanderbilt University, both in chemical engineering. She joined the faculty of the Georgia Institute of Technology in the School of Chemical & Biomolecular Engineering in August 2009 and is now Associate Professor and Marvin R. McClatchey and Ruth McClatchey Cline Faculty Fellow. Her research involves the design and synthesis of next-generation multifunctional, porous materials for adsorption applications.

Meilin Liu

Meilin Liu is a Regents' Professor of Materials Science and Engineering and Co-Director of the Center for Innovative Fuel Cell and Battery Technologies at Georgia Institute of Technology, Atlanta, Georgia, USA. He received his BS from South China University of Technology and both MS and Ph.D. from University of California at Berkeley. His research interests include insitu/operando characterization and multi-scale modeling of charge and mass transfer along surfaces, across interfaces, and in membranes, thin films, and nanostructured electrodes, aiming at achieving rational design of materials and structures with unique functionalities for efficient energy storage and conversion.