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Porous $NiMoO_4$-NrGO as a Battery-Like Electrode Material for Aqueous Hybrid Supercapacitors

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Supplementary

Materials and methods

The primary chemical materials used in this research along with their specifications are listed in Table S1.

Table S1. The primary chemicals used in this work.

No.	Chemical	Material Formulation	Source	Purity
1	Nickel (II) nitrate hexahydrate	$Ni(NO_3)_2.6H_2O$	Merck	99%
2	Sodium molybdate dihydrate	$Na_2MoO_4.2H_2O$	Merck	99%
3	Nickel	Ni foam	Latech Scientific Supply	85%
4	Corn starch	$(C_6H_{10}O_5)_n$	Sigma-Aldrich	-
5	Acetone	C_3H_6O	VWR	99.5%
6	Hydrochloric acid	HCl	VWR	90%
7	Ethanol	C_2H_6O	VWR	100%
8	Distilled water	DI H_2O	-	99.9%
9	Potassium hydroxide	KOH	VWR	99.9%
10	Graphene oxide	Go	Sigma-Aldrich	95%
11	Argon	Ar		99%
12	Polyvinylidene fluoride	$PVDF/(C_2H_2F_2)_{n-}$	Sigma-Aldrich	-
13	Dimethylformamide	DMF/C_3H_7NO	Sigma-Aldrich	99.8%
14	Carbon black	C	Sigma-Aldrich	99%
15	Ammonia	NH_3	VWR	28%

The electrochemical performance of the supercapacitor is estimated by using the CV and GCD curves as follows [1,2]:

$$C_{s,CV} = \frac{1}{m\nu\Delta V}\int IdV \quad (1)$$

$$C_{s,GCD} = \frac{\int Idt}{m\Delta V} \quad (2)$$

where Q [Cg^{-1}], dV, m [g], ν [mVs^{-1}], I [A], dt [s] are respectively attributed to the charge stored, potential window, mass loading of the active material, the scan rate, the discharge current and the discharge time.

To make an asymmetric supercapacitor, activated carbon electrode (AC), NMO-NrGO electrode, and cellulose paper were used respectively, as a negative electrode, positive electrode, and separator. To prevent irreversible reactions in negative and positive electrodes and obtain the maximum voltage window, the charge stored in both positive and negative electrodes must be equal. For this equality, the ratio of the mass placed on the positive and negative electrode is determined based on the charge balance theory equation [3,4].

$$m_+ \times Q_+ = m_- \times Q_- \quad (3)$$

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (4)$$

Where Q [Cg^{-1}] is the charge stored in each electrode, m [g] is the mass of the electroactive material and C [Fg^{-1}] is the specific capacitance of the electroactive material, and ΔV [V] is the voltage window of each electrode.

The energy density (E) and the power density (P) are calculated base on the following equations (5) and (6) [5]:

$$E = \frac{1}{2}C(\Delta V)^2 \quad (5)$$

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

Material characterization of $NiMoO_4$

The Energy dispersive X-ray (EDX) mapping analysis of $NiMoO_4$ is illustrated in Figure S1. It shows that $NiMoO_4$ is consisted of Mo, Ni and O elements.

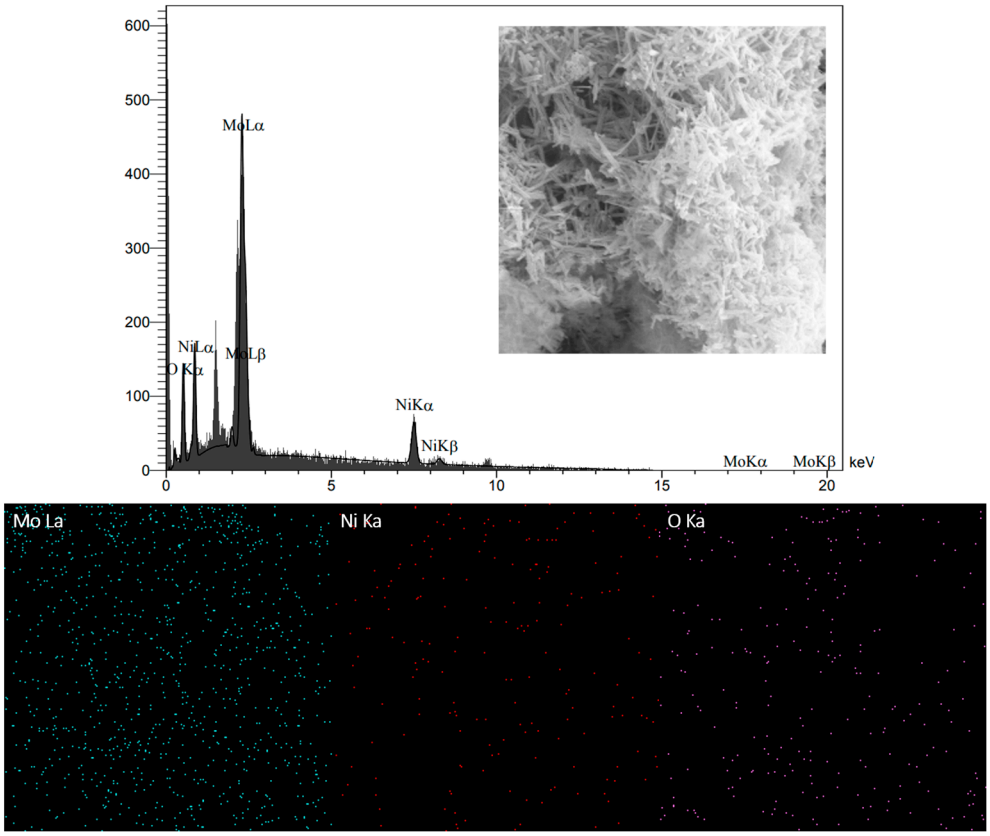


Figure S1. The Energy dispersive X-ray (EDX) mapping analysis of $NiMoO_4$.

Electrochemical properties of the optimized electrode of NMO-NrGO

Based on the electrochemical performance, all the results show that the NMO-NrGO electrode material gives better results than does the NMO-rGO electrode material for use in the supercapacitor; electrolyte optimization was also carried out for the NMO-NrGO electrode.

To investigate the effect of pH on the electrochemical behavior of the NMO-NrGO electrode, different types of electrolytes, such as acidic (H_2SO_4), alkaline (KOH), and neutral (Na_2SO_4) electrolytes, were studied at 3.0 M concentrations. For this purpose, the CV curves were measured at a scan rate of 10 mV s^{-1} for the NMO-NrGO electrode and the obtained results are shown in Figure S2a. Based on the CV curve of the H_2SO_4 electrolyte, a reduction peak is not observed, which shows that the NMO-NrGO electrode exhibits a high discharge rate in the H_2SO_4 electrolyte. It is also possible that the long-term use of acidic electrolytes in supercapacitor cells may cause corrosion in the Ni foam and reduce the lifetime of the electrodes. In the CV curve of the NMO-NrGO electrode in the Na_2SO_4 neutral electrolyte, very weak redox peaks were observed. As can be seen, the CV curve of the NMO-NrGO electrode obtained in the KOH electrolyte has a more symmetrical shape than do the curves obtained in the other electrolytes. This indicates the good reversibility of the electrode in KOH electrolyte, which could be due to the high redox reaction in KOH electrolyte [6]. In addition, K^+ ions (73.5 S·cm^2) have higher ionic conductivity than do Na^+ ions (50.11 S·cm^2), while OH^- ions (198 S·cm^2) have the highest ionic conductivity among other anions, including SO_4^- ions (160.0 S·cm^2) [7,8]. On the other hand, the KOH electrolyte has high ionic conductivity, has high mobility of OH^- ions, and, due to

the small size of OH^- ions (1.76 Å), can be used as a suitable electrolyte in most supercapacitors [7]. The specific capacitance of the NMO-NrGO electrode in the KOH electrolyte is about 495.7 Fg^{-1} at a scan rate of 10 mV s^{-1}; under similar conditions, its specific capacitances in H_2SO_4 and Na_2SO_4 electrolytes are calculated to be about 408 Fg^{-1} and 426 Fg^{-1}, respectively. Therefore, the results indicate that the NMO-NrGO electrode has the highest specific capacitance in alkaline electrolyte and the lowest in acidic electrolyte.

To optimize the electrolyte concentration to use in the whole supercapacitor cell, the KOH electrolyte was utilized at concentrations of 1.0, 2.0, 3.0, and 4.0 M. Figure S2b shows the obtained CV curves. As can be seen, the area under the CV curve for the NMO-NrGO electrode is greater in 3.0 M KOH electrolyte than at 1.0 M and 2.0 M concentrations, which indicates the higher specific capacitance of the electrode in 3.0 M KOH electrolyte than in the other two electrolytes. Also, at low concentrations, the activity of redox reactions is slightly lower, leading to a decrease in the cathodic and anodic currents of the NMO-NrGO electrode in 1.0 M and 2.0 M concentrations. The oxidation–reduction peaks of the NMO-NrGO electrode in 3.0 M KOH electrolyte are sharper and have a smaller potential difference than in the lower-concentration electrolytes. However, the CV curves in 3.0 M and 4.0 M KOH electrolytes are similar and almost overlapping. This shows that these two concentrations make little difference in the capacitance of the electrode, and that using a 4.0 M concentration simply wastes material. Furthermore, according to the observations, using high-concentration electrolytes (>4.0 M) corrodes the surface of the electrode substrate and eventually leads to the shedding (peeling) of electroactive materials from the substrate surface. Therefore, it is essential to optimize the electrolyte concentration, as it will have a great impact on the supercapacitor performance, especially the electrode life. The optimum concentration of the KOH electrolyte was considered to be 3.0 M.

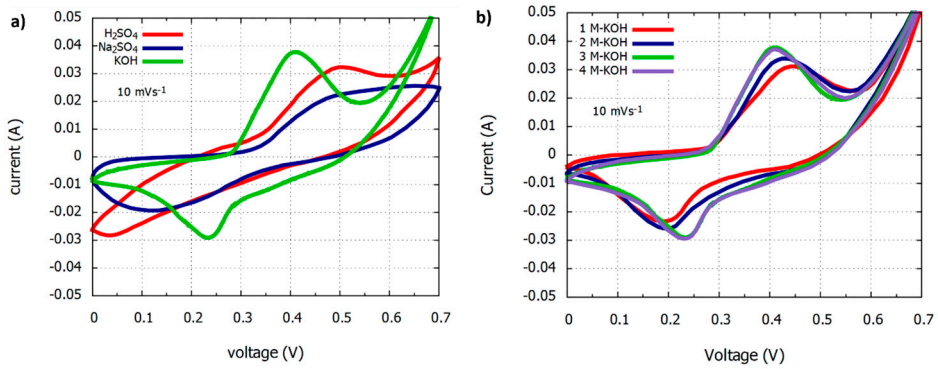


Figure S2. CV curves of the NMO-NrGO electrode: (**a**) in 3.0 M H_2SO_4, 3.0 M KOH, and 3.0 M Na_2SO_4 electrolytes; (**b**) in KOH electrolyte with concentrations of 1.0, 2.0, 3.0, and 4.0 M.

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