

Electronic Supplementary Information

Efficient Metal Recovery and Electrocatalyst Fabrication from Spent Lithium-Ion via Green Solvent Extraction

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Number of pages: 36

Number of Figures: 20

Number of tables: 7

Table of Contents

Item	Caption	Page No
Experimental section	Raw materials, Fabrication of nickel cobalt sulfide, Reemployment of the DES and enrichment of manganese and lithium, Characterizations, Electrochemical Measurements, Density functional theory calculations	S4
Fig. S1	Photograph, XRD pattern, SEM image of the S-NCM	S8
Fig. S2	FT-IR spectra of Chcl and CA	S9
Fig. S3	Binding energy of DES components and metal atoms	S10
Fig. S4	Charge density difference of electron transfer from CA to metal sites on S-NCM	S11
Fig. S5	UV-vis spectra and Photographs of P-DES	S12
Fig. S6	FT-IR spectra and pH tests of recycled DES	S13
Fig. S7	XRD pattern and SEM image of MnC_2O_4	S14
Fig. S8	SEM image of CFP	S15
Fig. S9	Magnifying SEM images of NCS-3 and NCS-5	S16
Fig. S10	EDS element spectra of NCS-1 and NCS-5	S17
Fig. S11	Nitrogen adsorption-desorption isotherms of NCS-1, NCS-3 and NCS-5	S18
Fig. S12	In-situ contact angle measurements of NCS-1, NCS-3, and NCS-5	S19
Fig. S13	The survey XPS spectra of NCS-1, NCS-3, and NCS-5	S20
Fig. S14	Reproducibility of NCS-3	S21
Fig. S15	Cyclic voltammetry curves of NCM-1, NCS-3, NCS-5, and RuO_2 .	S22
Fig. S16	ECSAs of the as-prepared electrodes for OER	S23
TOF calculation	TOF calculation for NCS-3	S24
Fig. S17	TOF of the as-prepared electrodes for OER	S24
Fig. S18	Generation of O_2 bubbles on NCS-3	S25
Fig. S19	EDS elemental spectra of NCS-3 after OER	S26
Fig. S20	SEM images of NCS-811 and NCS-523	S27
Table S1	Elemental composition of the $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$	S28
Table S2	DES stability and metal extraction efficiency over	S29

	multiple recycling cycles	
Table S3	Elemental composition of nickel cobalt sulfides	S30
Table S4	Elemental composition of nickel cobalt sulfides based on EDS and ICP analysis	S31
Table S5	The comparison of the OER performances of NCS-X and RuO ₂	S32
Table S6	OER Rate-determining step (RDS) determined by Tafel slope in alkaline electrolyte	S33
Table S7	Comparison of the OER performance of NCS-3 with recently reported electrocatalysts	S34

Experimental section

Raw materials: The spent lithium-ion batteries with $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (NCM) cathode were first discharged in a 10 % NaCl solution and followed by manual dismantlement. Then, the positive plate was heated at 450 °C for 3 h to strip the black powders of the NCM cathode from the aluminum foils. Choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$, ChCl, 98 %), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, CA, 99 %), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, OA, 99 %), thioacetamide (CH_3CSNH_2 , TAA, 98 %) and KOH (98 %) are analytical grade from Aladdin. Carbon fiber paper (surface density: 0.44 g cm^{-3}) was purchased from TORAY.

Fabrication of nickel cobalt sulfide (NCS-X): First, 60 mmol ChCl (8.38 g) and 60 mmol CA (12.61 g) were dissolved in 6 mL of water to obtain ChCl-CA-based DES solution. Then, 0.18 g (1.88 mmol) of as-prepared NCM raw material was added to DES solution under agitating at 90 °C for 2 h. When the solution temperature cooled to room temperature, a certain amount of TAA (1.88, 5.63 and 9.39 mmol) was mixed in DES solution, which was then placed into a 50 mL Teflon-lined reactor. Afterward, the pre-washed carbon fiber paper (CFP) ($1.5 \times 3 \text{ cm}$) was immersed into the precursor solution, followed by the solvothermal process for 9 h at the temperature of 160 °C. Finally, the nickel cobalt sulfide (NCS-X, X=1, 3, 5, X represents the molar ratio of TAA to NCM) electrode was obtained after water-washing and desiccating at 60 °C for 24 h under vacuum. The mass loading of NCS-1, NCS-3, and NCS-5 was measured as 2.8, 3.2, and 3.1 mg cm^{-2} .

Reemployment of the DES and enrichment of manganese and lithium: The used DES was heated to remove water and reused in the next cycle. Then, enriched manganese element can be precipitated via the addition of oxalic acid. For lithium recovery, the lithium element is obtained in the form of LiC_2O_4 by evaporating the remaining solution to dryness and washing it with ethanol.

Characterizations: The microstructure and elemental distribution were verified by field-emission scanning electron microscopy (SEM, JEOL 7610F) and transmission electron microscopes (TEM, JEM F200). The phase structures of catalytic electrodes were explored by X-ray diffraction (XRD) patterns (Rigaku smartlab, $\text{Cu-K}\alpha$). The UV-Vis absorption spectra were conducted in a UV-vis spectrophotometer (Shimadzu UV-1800). XPS measurements (Thermo Fisher Scientific K-Alpha) were applied to ascertain the chemical constitution. Fourier-transform infrared (FT-IR) spectra were collected using a VERTEX 80/80V FT-IR spectrometer. N_2 adsorption-desorption isotherms (Autosorb iQ2-C-TPX) were employed to evaluate the surface area and pore structure of NCS-X electrodes. The metallic element composition of NCS-X electrodes was detected by ICP-OES (Thermo Fisher iCAP 7400). Dynamic contact angles of the NCS-X electrodes were measured at 25 °C (Dataphysics OCA25).

Electrochemical Measurements: All electrochemical characteristics were performed on an electrochemical station (CHI760E) in 1 M KOH solution based on a three-electrode system (the as-prepared samples (1.0 cm × 1.0 cm), the graphite rod

(d=6 mm) and the Hg/HgO electrode). All potentials in this study were gauged by reversible hydrogen electrode (RHE) potentials according to the following equation:

$$E_{vsRHE} = E_{Hg/HgO} + 0.098 + 0.059 \times \text{pH}$$

Linear sweep voltammetry (LSV) tests were carried out at 1.1 V to 1.8 V at 5 mV s⁻¹. Tafel slopes were calculated from the corresponding LSV curves. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.01 Hz to 100 kHz. The electrochemical active area was tested and calculated at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹ with a potential range from 1.1 to 1.2 V vs. RHE.

Density functional theory calculations: To determine the binding energies between Citric acid and Ni, Co, Mn on the NCM surface, as well as the binding energies between chloride ions and these metals in various oxidation states. All calculations were carried out by using the projector augmented wave (PAW)¹ method in the framework of the density functional theory (DFT), as implemented in the Vienna ab-initio Simulation Package (VASP).² The generalized gradient approximation (GGA) exchange-correlation function was profiled by the Perdew-Burke-Ernzerhof (PBE).³ In the vertical direction, a vacuum layer of about 15 Å in thickness was introduced for all the surfaces to avoid periodic interactions. The energy cutoff for plane-wave expansion of the PAWs is 520 eV. The convergence criteria of energy and force calculations were set to 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. The integration of the Brillouin zone was performed using a Gamma-center mesh of 1 × 3 × 1 k-points.

The adsorption energy (E_{ads}) of adsorbates was calculated according to

$$E_{ads} = E(total) - E(substrate) - E(adsorbate) \#(1)$$

Where $E(total)$, $E(substrate)$ and $E(adsorbate)$ represent the energies for adsorbed systems, NCM substrates, and isolated adsorbates, respectively. According to this definition, the more negative the E_{ads} value, the stronger the adsorbent interacts with the substrates.

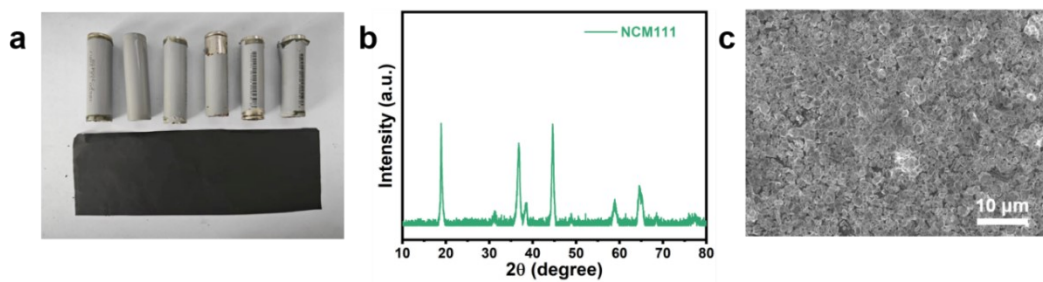


Fig. S1 (a) Photograph (b) XRD pattern and (c) SEM image of the S-NCM.

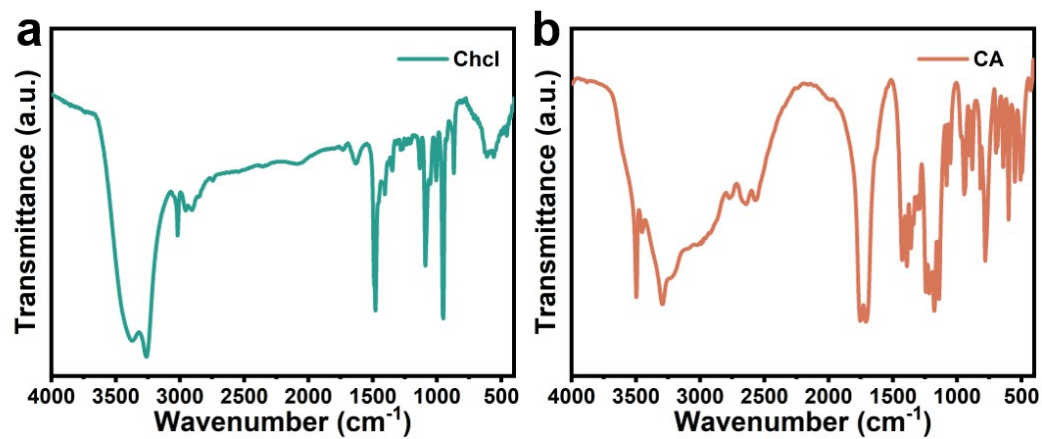
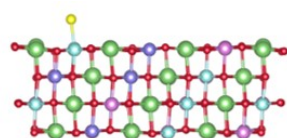
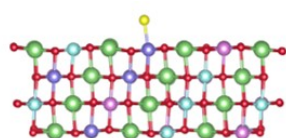


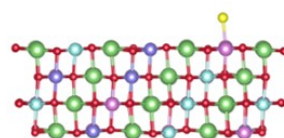
Fig. S2 FT-IR spectra of (a) Chcl and (b) CA.



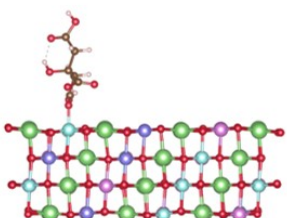
Cl-Ni: -0.83 eV



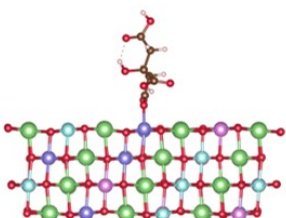
Cl-Co: -1.23 eV



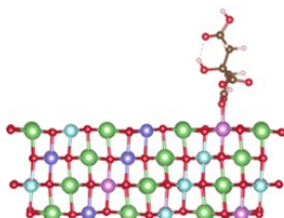
Cl-Mn: -1.39 eV



CA-Ni: -2.26 eV



CA-Co: -2.74 eV



CA-Mn: -2.83 eV

Fig. S3 Binding energy of Cl^- and CA with metal atoms on the surface of S-NCM.

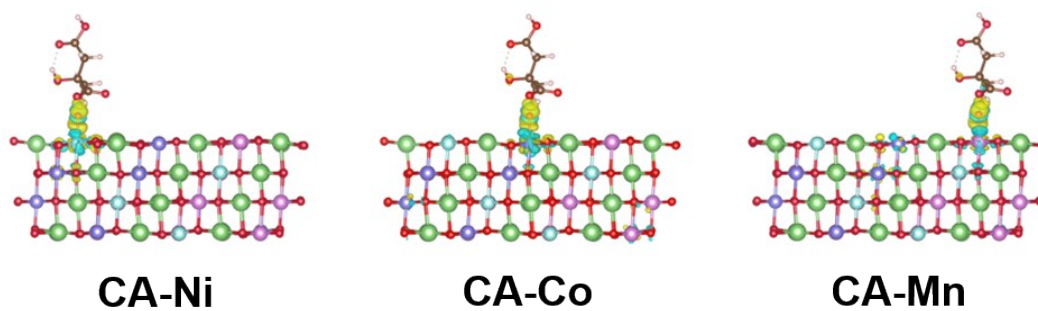


Fig. S4 The charge density difference of electron transfer from CA to metal sites on S-NCM.

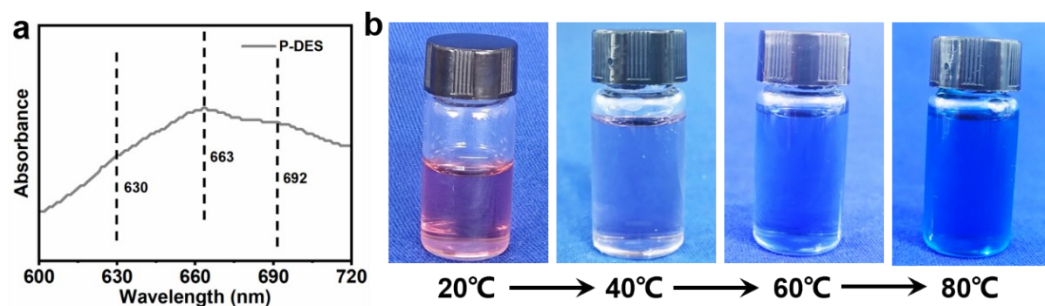


Fig. S5 (a) UV-vis spectra of P-DES. (b) Photographs of the color change during S-NCM cathode powder dissolution in the DES from different temperatures.

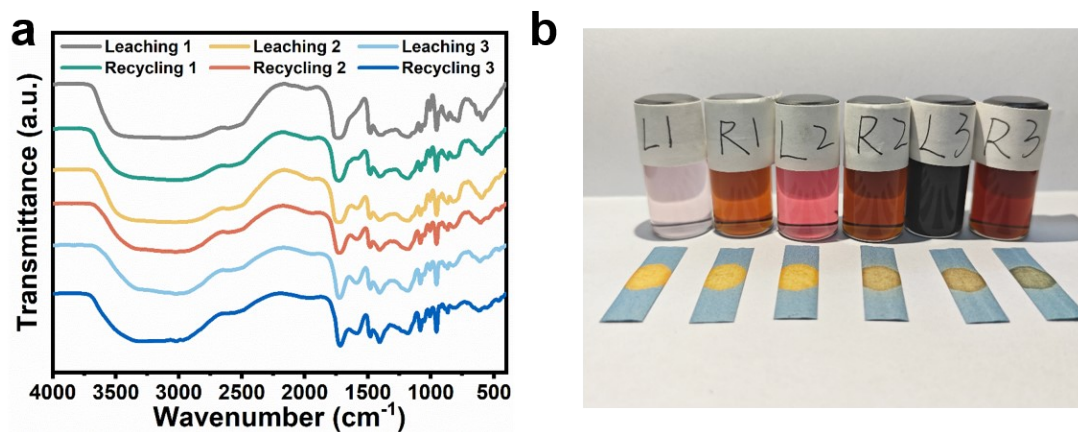


Fig. S6 (a) FT-IR spectra and (b) pH tests of recycled DES.

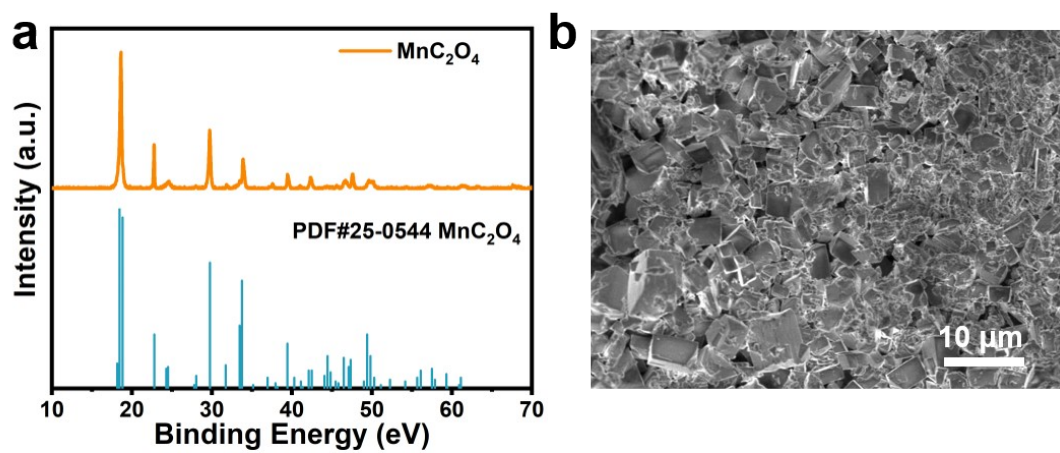


Fig. S7 (a) XRD pattern and (b) SEM image of the recycling MnC₂O₄.

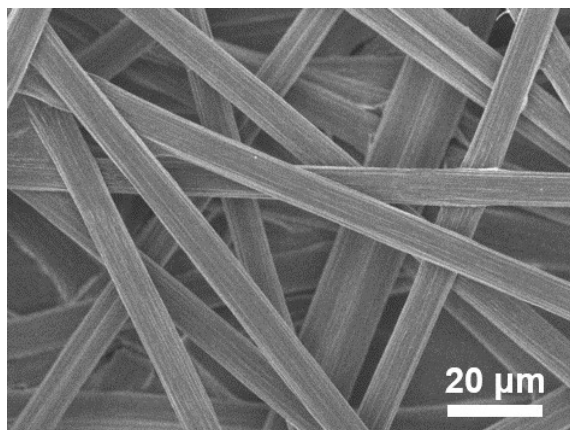


Fig. S8 SEM image of CFP.

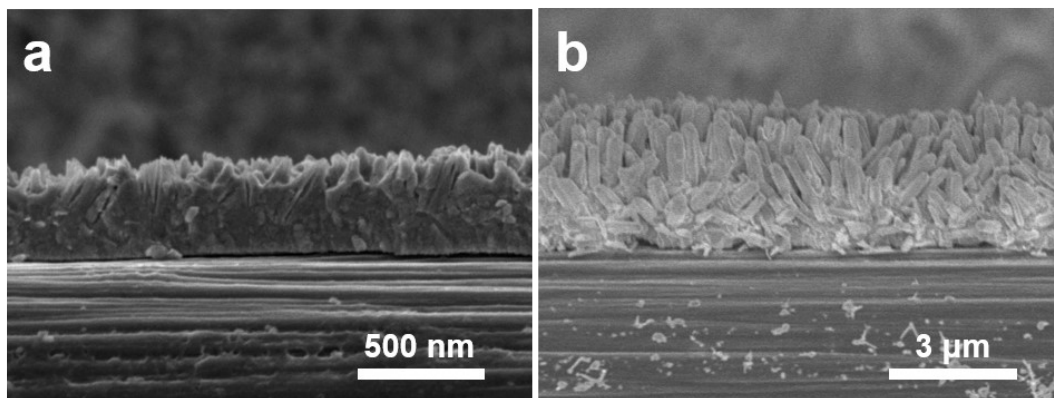


Fig. S9 The magnifying SEM images of (a) NCS-3 and (b) NCS-5.

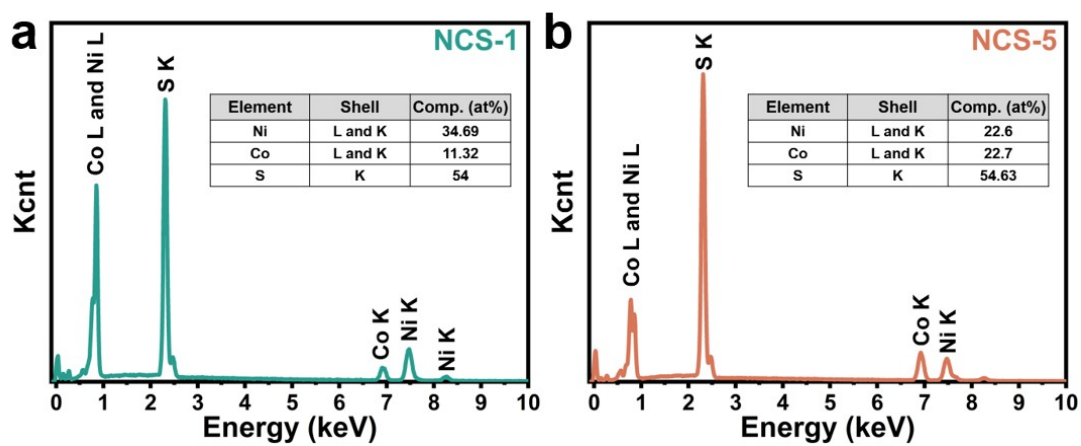


Fig. S10 EDS element spectra and corresponding relative contents of different elements (a) NCS-1 and (b) NCS-5.

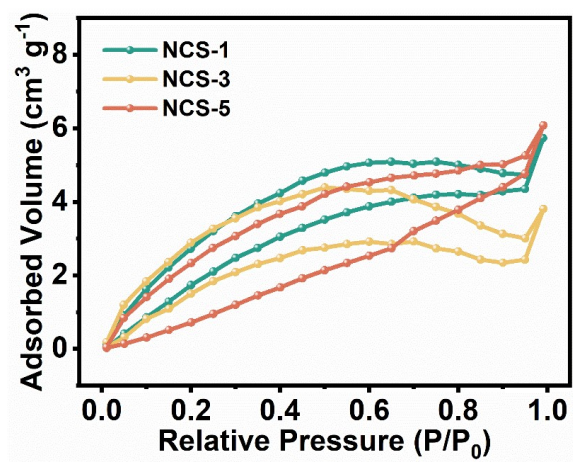


Fig. S11 Nitrogen adsorption-desorption isotherms of NCS-1, NCS-3 and NCS-5.

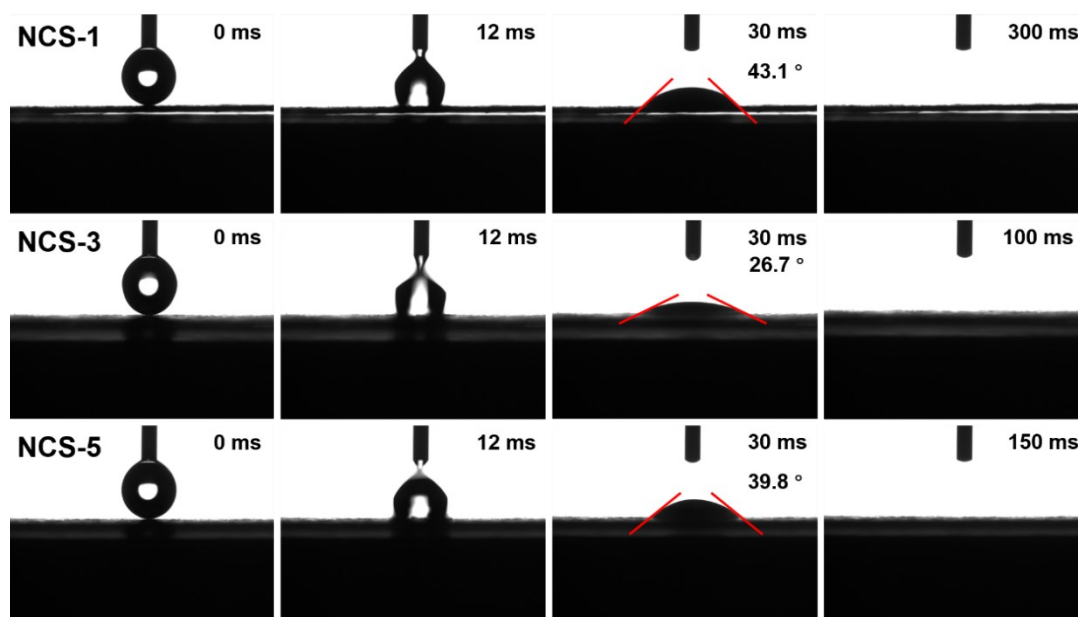


Fig. S12 In-situ contact angle measurements of NCS-1, NCS-3, and NCS-5.

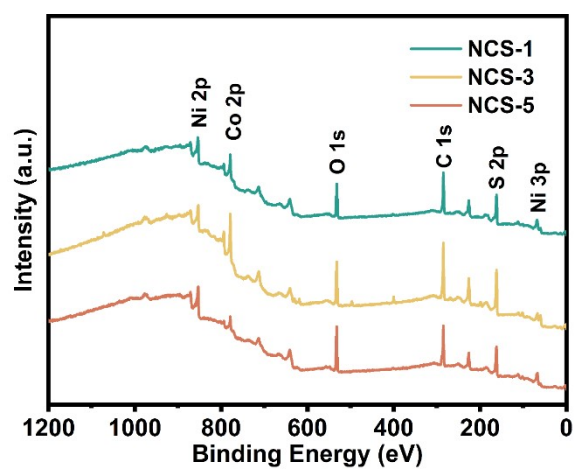


Fig. S13 The survey XPS spectra of NCS-1, NCS-3, and NCS-5.

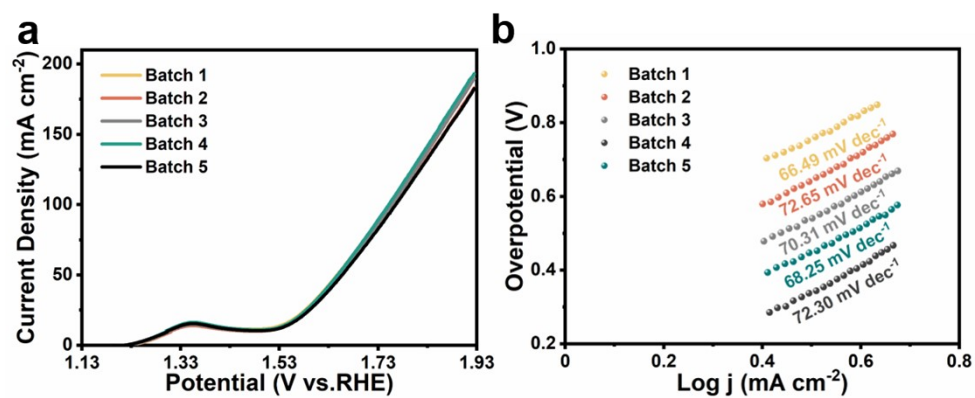


Fig. S14 Reproducibility of NCS-3. (a) LSV curves and (b) Tafel slopes of NCS-3 made from different batches of spent $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cathodes.

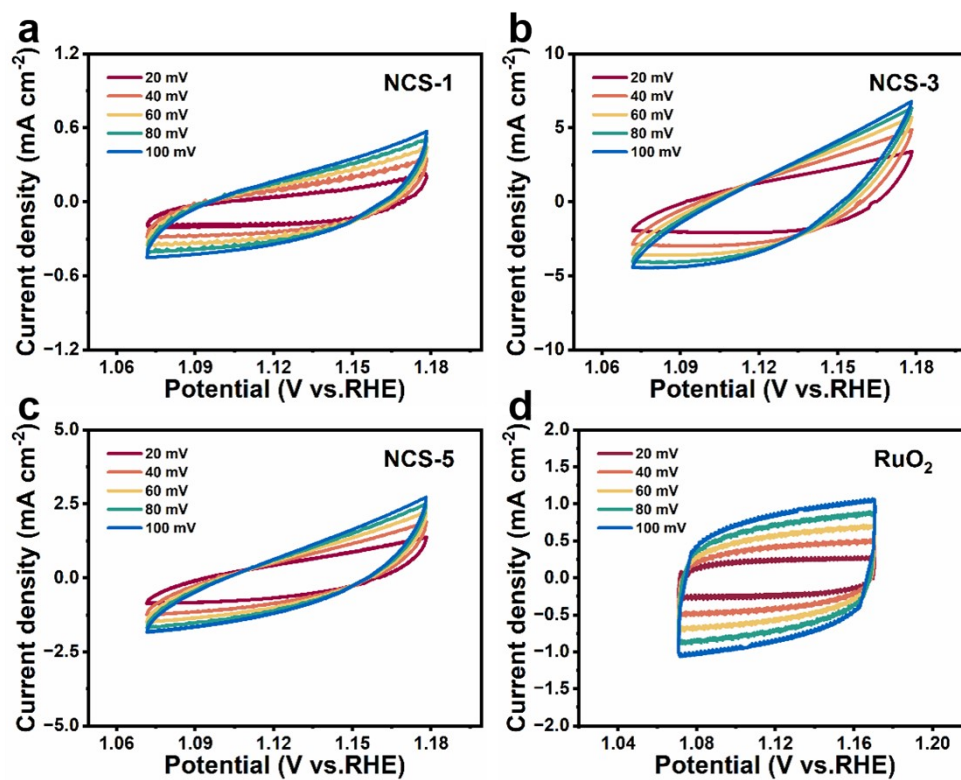


Fig. S15 Cyclic voltammetry curves of (a) NCM-1, (b) NCS-3, (c) NCS-5, (d) RuO_2 .

Electrochemically active surface area (ECSA) calculation on OER

The ECSAs of all as-prepared electrodes were calculated through the C_{dl} values in the non-Faradic region with different CV scan rates of 20~100 mV s⁻¹. The ECSA had a fixed proportion to C_{dl} as the below equation (2) shown^{4,5}:

$$ECSA = \frac{C_{dl}}{C_s} \#(2)$$

Where C_s was the specific capacitance of 0.040 mF cm⁻².

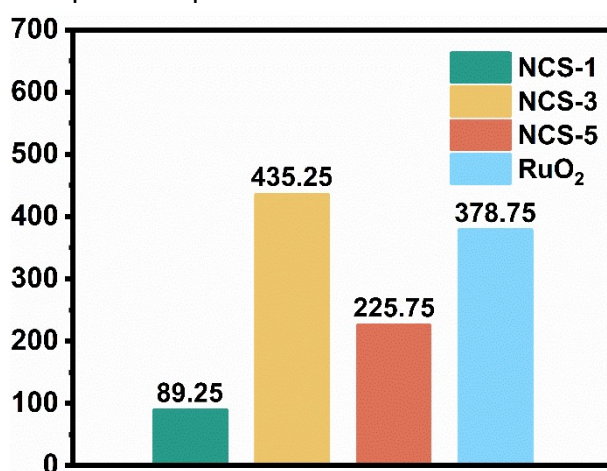


Fig. S16 ECSAs of the as-prepared electrodes for OER.

TOF calculation for NCS-3 on OER

The TOF of per site in NCS-3 was calculated by the below equation (3):

$$TOF = \frac{\text{number of } O_2 \text{ turn overs/cm}^2 \text{ geometric area}}{\text{number of active sites/cm}^2 \text{ geometric area}} \quad \#(3)$$

$$\text{number of } O_2 = (j \frac{mA}{cm^2}) (\frac{1 C s^{-1}}{1000 mA}) (\frac{6.02 \times 10^{23} O_2 \text{ molecules}}{1 mol O_2}) (\frac{1 mol e^-}{96485 C}) (\frac{1 mol O_2}{4 mol e^-})$$

$$= 1.56 \times 10^{15} \frac{O_2 s^{-1}}{cm^2} \text{ per } \frac{mA}{cm^2}$$

The Ni and Co sites were all found to be the active sites for OER in previous literatures. According to the SEM-EDS result, the Ni wt% and Co wt% were 33.00% and 27.63%, respectively. The electrodeposited mass of NCS-3 was weighted as 3.2 mg cm⁻². Therefore, the number of active sites (Ni and Co) could be calculated via the below equation (4)^{4,5}:

$$\text{number of active sites} = \left(\frac{33.00}{58.63} + \frac{27.63}{58.93} \right) \times \frac{1 \text{ mmol}}{100 \text{ mg}} \times 3.2 \frac{\text{mg}}{\text{cm}^2} \times 6.02 \times 10^{20} \frac{\text{site}}{\text{mmol}} \quad \#(4)$$

$$= 1.99 \times 10^{19} \text{ sites cm}^{-2}$$

The OER current densities of NCS-3 at the overpotential of 250, 300 and 350 mV were 10.04, 15.01, and 29.01 mA cm⁻², respectively. Therefore, the O₂ TOF under these overpotentials were calculated as 0.00131, 0.00196 and 0.0379 s⁻¹, respectively.

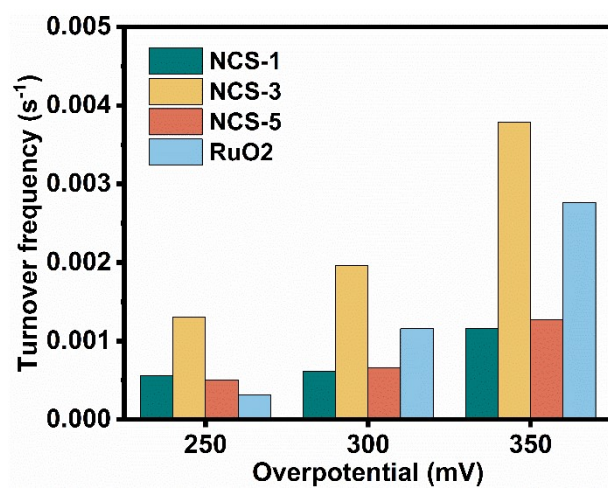


Fig. S17 TOF of the as-prepared electrodes for OER at different overpotentials.

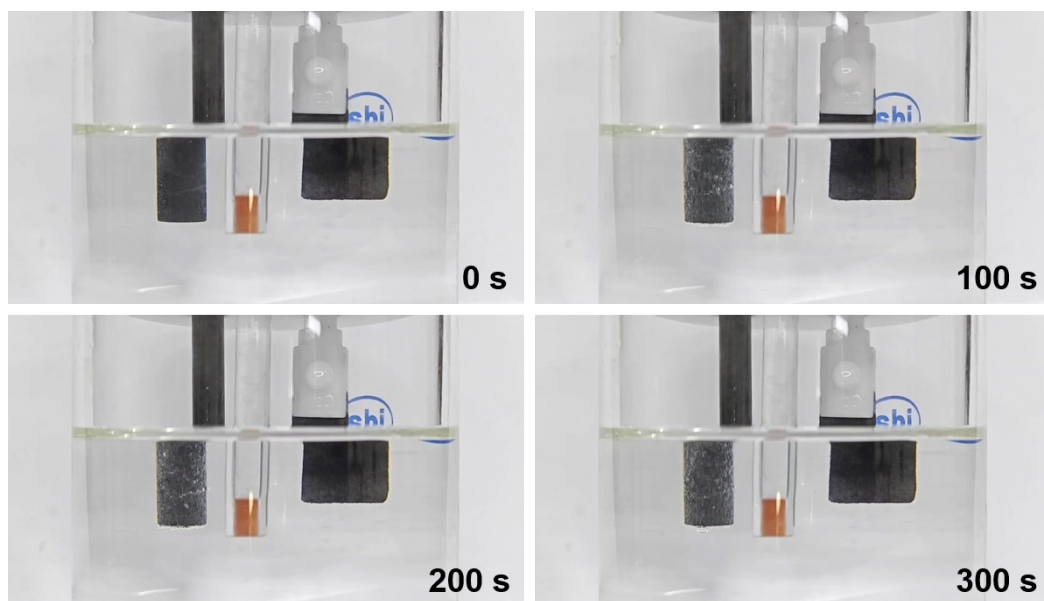


Fig. S18 Generation of O₂ bubbles on NCS-3 with a constant current density of 10 mA cm⁻².

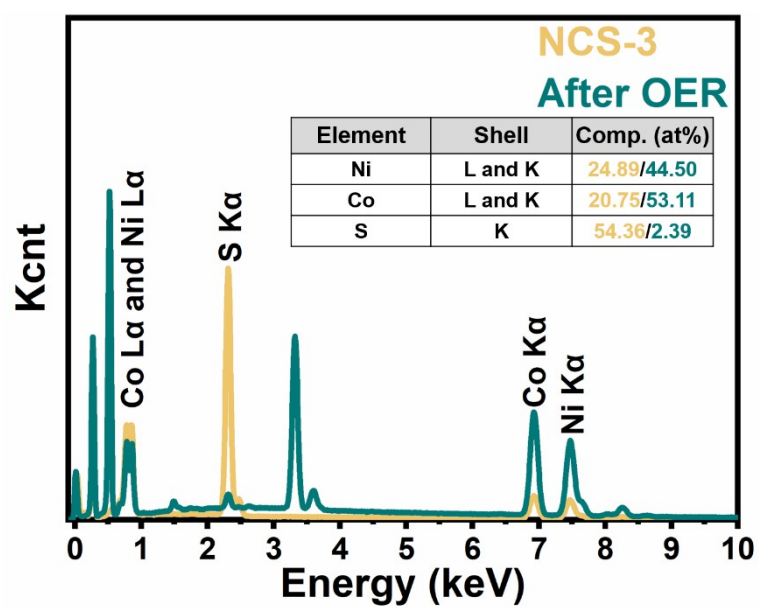


Fig. S19 EDS elemental spectra of NCS-3 after OER and the corresponding relative contents of different elements.

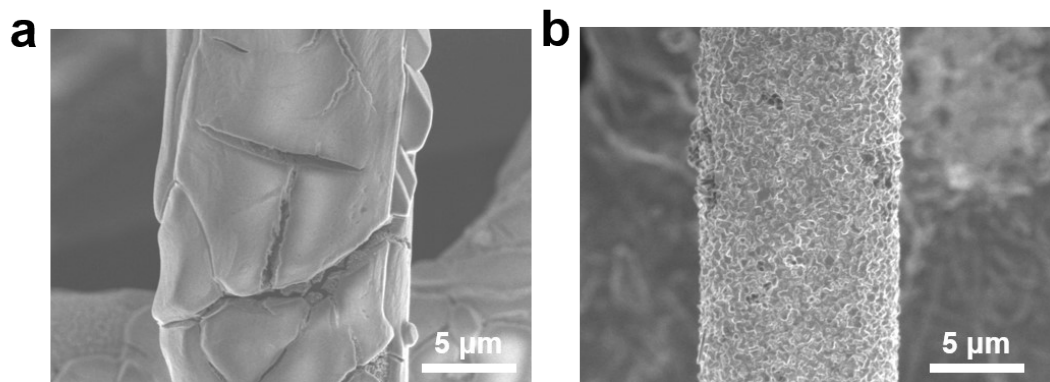


Fig. S20 SEM images of (a) NCS-811 and (b) NCS-523.

Table S1. Elemental composition of the $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$.

Content	Ni	Co	Mn
Composition(wt%)	38.76	37.57	23.67
Composition(at%)	38.21	36.86	24.93

Table S2. DES stability and metal extraction efficiency over consecutive recycling cycles.

Cycle	Ni Leaching (%)	Co Leaching (%)	Mn Leaching (%)
Leaching 1	98.24	98.22	97.39
Recycling 1	0.02	0.01	99.68
Leaching 2	97.95	97.87	96.93
Recycling 2	0.01	0.02	99.72
Leaching 3	97.79	97.75%	96.75
Recycling 3	0.01	0	99.57

Table S3. Elemental composition of nickel cobalt sulfides based on ICP analysis.

	Ni/Co/Mn		
	NCS-1	NCS-3	NCS-5
Composition (wt.%)	78.83/21.13/0.04	57.51/42.46/0.02	49.59/50.38/0.03
Composition (at.%)	78.90/21.06/0.04	57.60/42.38/0.02	49.70/50.27/0.03

Table S4. Elemental composition of nickel cobalt sulfides based on EDS and ICP analysis.

	Ni/Co/S		
	NCS-1	NCS-3	NCS-5
ICP	2.4/0.6/3.5	1.7/1.3/3.5	1.5/1.5/3.6
EDS	2.3/0.7/3.5	1.7/1.3/3.5	1.5/1.5/3.6

Table S5. The comparison of the OER performances of NCS-X and RuO₂.

Electrode	Overpotential (mV)	Tafel Slope (mV dec ⁻¹)	R _{ct} (Ω)	C _{dl} (mF cm ⁻²)	ECSA	TOF@300 mV (s ⁻¹)
NCS-1	335@10 mA	72.68	4.6	3.57	89.25	6.11×10 ⁻⁴
NCS-3	248@10 mA	67.74	2.4	17.41	435.25	1.96×10⁻³
NCS-5	302@10 mA	76.96	3.4	9.03	225.75	6.59×10 ⁻⁴
RuO ₂	321@10 mA	86.45	7.7	15.15	378.75	1.16×10 ⁻³

Table S6. OER rate-determining step (RDS) determined by Tafel slope in alkaline electrolyte.⁶

Step	RDS	Tafel slope (mV dec ⁻¹)
1	$M + OH^- \leftrightarrow M-OH + e^-$	120
2	$MOH + OH^- \leftrightarrow MO^- + H_2O$	60
3	$MO^- \leftrightarrow MO + e^-$	40
4	$2MO \leftrightarrow 2M + O_2$	15

For NCS-3 catalysts, the reaction mechanism for OER is as follows. Firstly, the OH⁻ is adsorbed on the active site of M to produce M-OH and an electron (Step 1, 120 mV dec⁻¹). Then, the OH⁻ is adsorbed on the M-OH is converted to the intermediate M=O and produces one H₂O and an electron (Step 2, 60 mV dec⁻¹). Subsequent adsorption of OH⁻ forms the redox active substance M-OOH and an electron (Step 3, 40 mV dec⁻¹). Finally, MOOH is oxidized and thus produces O₂, H₂O and an electron (Step 4. 15 mV dec⁻¹). In our NCS-3 catalyst, MOOH (M = Ni and Co) is the active site for electrocatalytic OER. The Tafel slope for NCS-3 is 67.74 mV dec⁻¹, which suggests that Step 2 is the rate-determining step.

Table S7. Comparison of the OER performance of NCS-3 with recently reported electrocatalysts.

Electrode	Electrolyte	Overpotential @10 mA cm ⁻² (mV)	Tafel Slope (mV dec ⁻¹)	Life (h/cycles)	Ref.
NCS-3	1 M KOH	248@10 mA	67.74	125 h	This work
NCS	1 M KOH	260@10 mA	68.41	100 h	7
CoNi-S-900@NCFs	1 M KOH	330@10 mA	49.08	2000 cycles	8
NiCo ₂ S ₄ -NiS ₂ /CFP	1 M KOH	165@10 mA	81.54	12 h	9
Au@NiCo ₂ S ₄	1 M KOH	299@10 mA	44.5	5 h	10
NiCoS	1 M KOH	338@10 mA	69.1	8 h	11
NCO@NCHy	1 M KOH	287@10 mA	106	6 h	12
Mo-NiCoO ₄	1 M KOH	265@10 mA	126.6	100 h	13
NC-2	1 M KOH	337@10 mA	67.3	30 h	14
NiCoO ₂ @NiCoLDH	1 M KOH	272@10 mA	75	12	15
Ni/NiCoO _x /NF	1 M KOH	292@10 mA	86.9	50	16
NiCoSe ₄ @CFF	1 M KOH	358@10 mA	115.93	16	17
NiCoSe S/BP	1 M KOH	285@10 mA	118	10	18
NCS _e	1 M KOH	323@10 mA	145	12	19
NiCo-Se@CNTs	1 M KOH	260@10 mA	138	10	20
NiCoSe@NF	1 M KOH	278@10 mA	92	48	21

References:

- [1] G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- [2] P.E. Blöchl and *Phys. Rev. B*, 1994, **50**, 17953–17979.
- [3] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- [4] M. Poudel, N. Logeshwaran, S. Prabhakaran, A. Kim, D. Kim and D. Yoo. *Adv. Mater.*, 2023, **36**, 2305813.
- [5] L. Wu, L. Yu, F. Zhang, B. McElhenny, D. Luo, A. Karim and S. Chen, *Adv. Funct. Mater.*, 2021, **31**, 2006484.
- [6] S. Sun, G. Sun, P. Cheng, R. Liu and C. Zhang, *Mater. Today Energy*, 2023, **32**, 101246.
- [7] Z. Yan, L. Wang, L. Wang, S. Tian, Y. Wei and J. Sun, *ACS Appl. Energy Mater.*, 2024, **7**, 10474-10486.
- [8] Y. Lv, S. Duan, Y. Zhu, P. Yin and R. Wang, *Nanomaterials*, 2020, **10**, 611.
- [9] X. Gong, H. Zhong, L.A. Estudillo-Wong, N. Alonso-Vante, Y. Feng and D. Li, *J. Energy Chem.*, 2022, **74**, 376-86.
- [10] J. Li, Y. Xia, X. Luo, T. Mao, Z. Wang, Z. Hong and G. Yue, *Coatings*, 2023, **13**, 313.
- [11] M. Kahnamouei and S. Shahrokhian, *ACS Appl. Energy Mater.*, 2022, **5**, 5199-5211.
- [12] M. Puthalath, A. Kunhiraman, A. Thangaraj, R. Rakkesh and S. Rakkesh, *J. Phys. Chem. Solids*, 2024, **192**, 112075.
- [13] Y. Tao, W. Jiang, H. Wang, W. Hao, Q. Bi, X. Liu, J. Fan and G. Li, *J. Phys. Chem. Solids*, 2024, **657**, 921-930.
- [14] N. Gultom, M. Silitonga, K. Hu, Y. Zhou and D. Kuo, *J. Alloys Compd.*, 2023, **955**, 170232.
- [15] Z. Wu, X. Hu, C. Cai, Y. Wang, X. Li, J. Wen, B. Li and H. Gong, *J. Colloid Interface Sci.*, 2024, **657**, 75-82.
- [16] G. Liu, A. Bao, C. Li, N. Zhou, C. Yang, X. Chen, Y. Li and D. Liu, *J. Alloys Compd.*, 2023, **847**, 169657.

- [17] L. Du, N. Lv, J. Li, J. Zhang, Y. Chen, Y. Zhang, Z. Li, X. Huang and J. Luo, *J. Ind. Eng. Chem.*, 2023, **120**, 467-476.
- [18] T. Liang, S. Lenus, Y. Liu, Y. Chen, T. Sakthivel, F. Chen, F. Ma and Z. Dai, *Energy Environ. Mater.*, 2023, **6**, 2575-0348.
- [19] V. Salarvand, M. Mohammadi, F. Ahmadian, F. Kouchi, M. Yazdi and A. Mostafaei, *J. Electroanal. Chem.*, 2022, **926**, 116929.
- [20] A. Ali, S. Muqaddas, H. Aldosari, S. Rashid, A. Hafiz, M. Saeed, A. Ahmad and M. Ahmad, *CARBON*, 2023, **218**, 118709.
- [21] Y. Zhou, Y. Chen, M. Wei, H. Fan, X. Liu, Q. Liu, Y. Liu, J. Cao and L. Yang, *CrystEngComm*, 2021, **23**, 69-81.