

Supplementary Information

Data-driven exploration of weak coordination microenvironment in solid-state electrolyte for safe and energy-dense batteries

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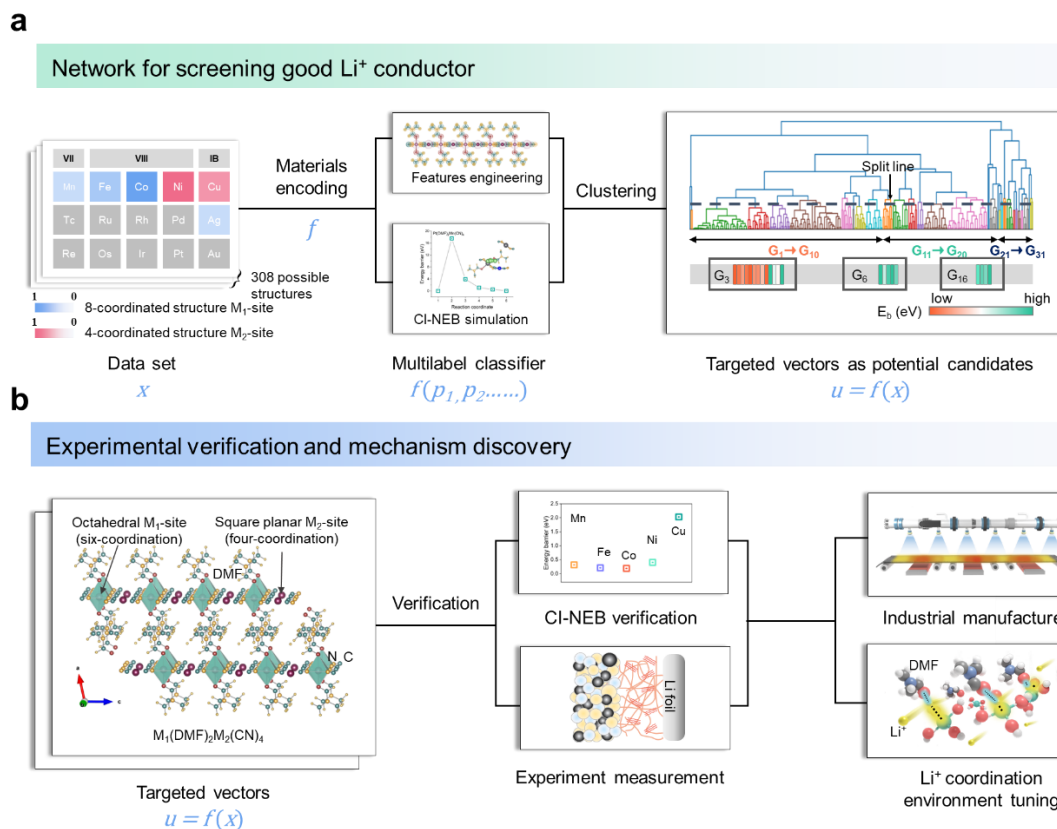
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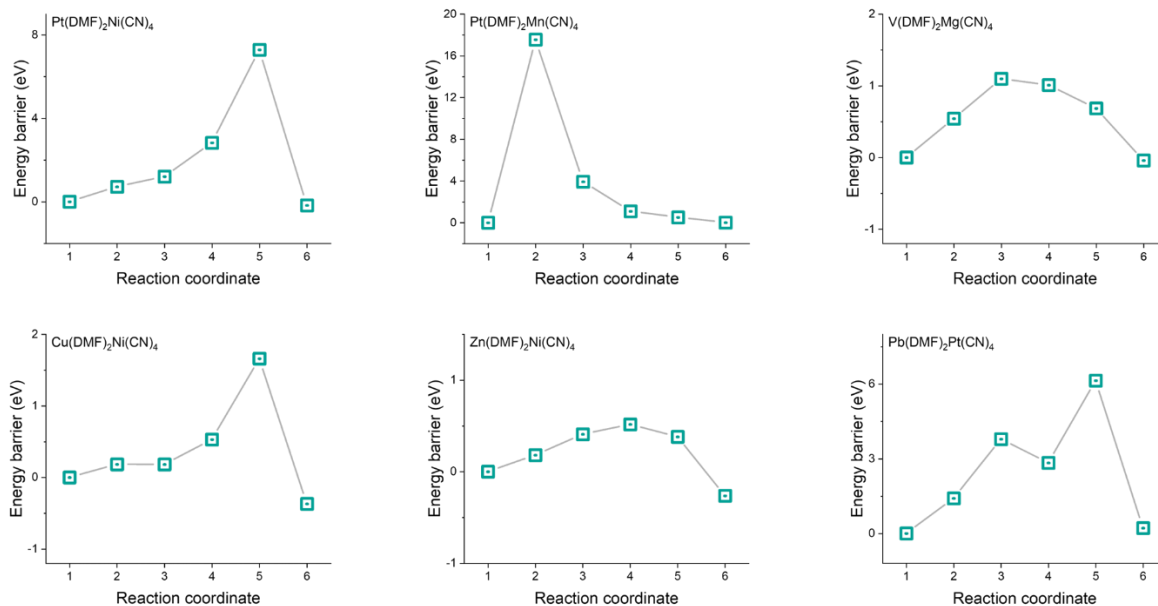
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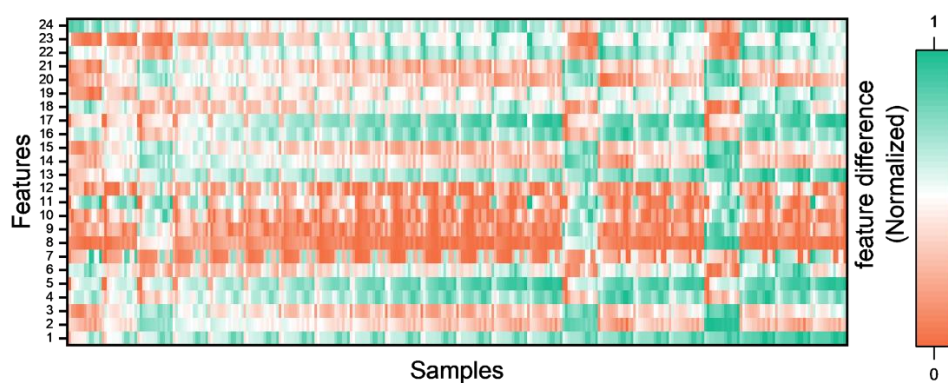
Supplementary figures and tables



Supplementary Fig. 1 | a, Workflow diagram of CI-NEB simulations assisted with ML methods screening fast Li^+ conductor. This includes generating a dataset by substituting metals in Hofmann complexes resulting in 308 different candidates, followed by applying unsupervised clustering to classify candidates based on their energy barriers for ion migration. **b, Workflow diagram of interpreting Li^+ coordination tuning to guide the solid-state electrolyte design.** Based on the prediction results, we selected and synthesized promising Hofmann complexes, and fabricated series M-Ni based electrolytes. DFT calculations and series experiments were conducted to investigate the ion transport behaviors. The main purpose is to discover the influence of the coordination environment by modulating the interaction with Li^+ , offering a rational understanding to help with the design of practical safe and energy-dense solid-state batteries.

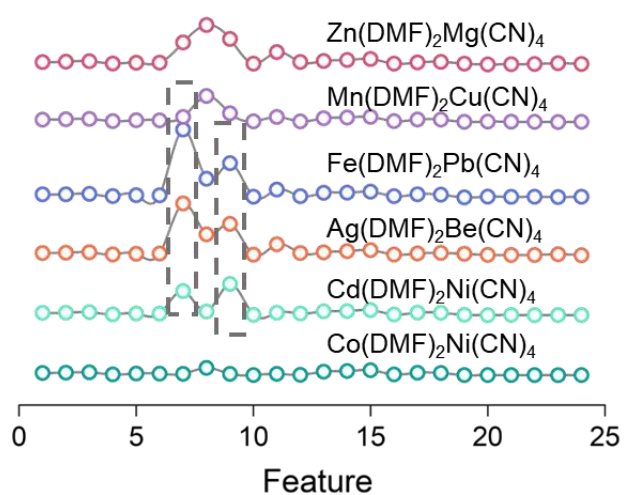


Supplementary Fig. 2 | Energy barrier of ion migration. CI-NEB simulations calculated the energy barrier of ion migration, which is used as assessment index.

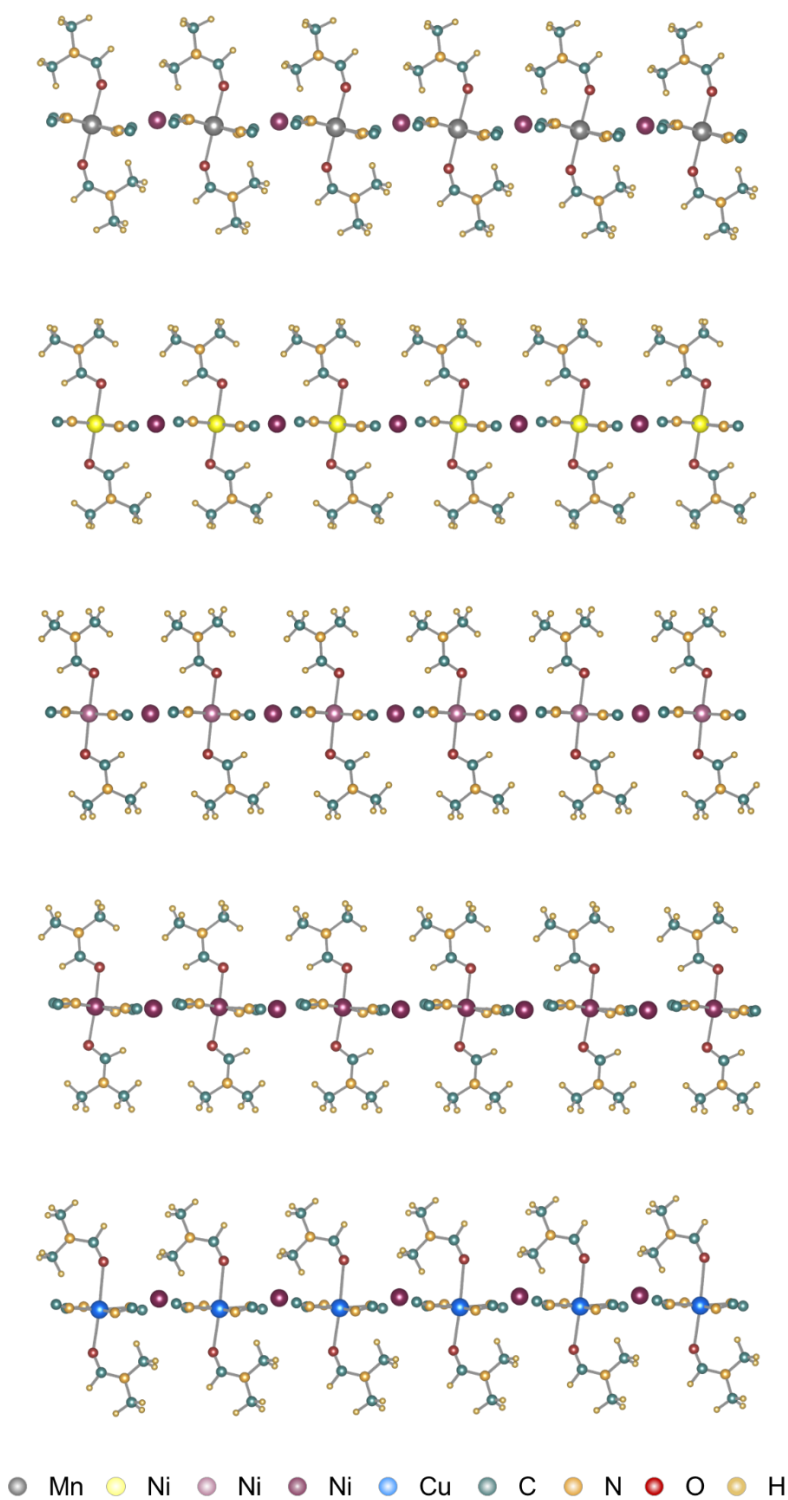


Supplementary Fig. 3 | Heat maps of the 24-dimensional feature vectors of 308 candidates.

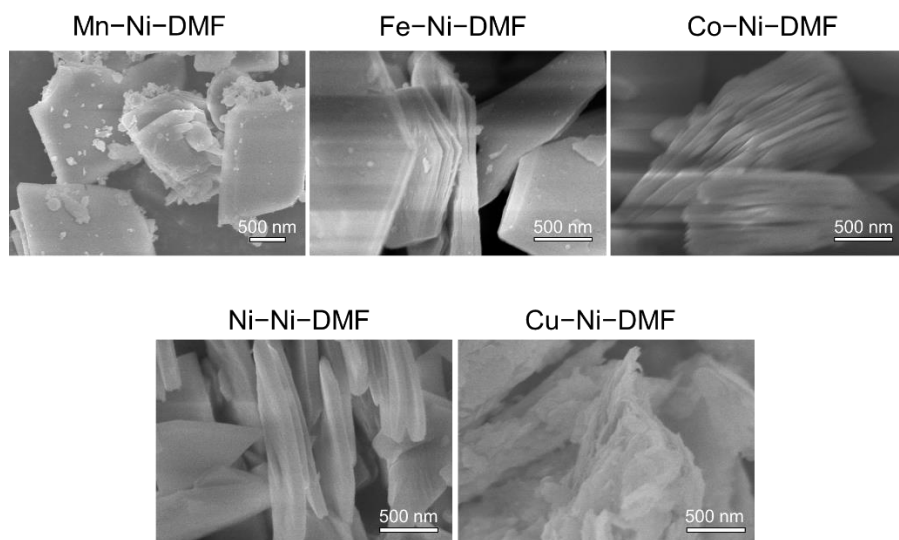
The color bars are the values of the calculated feature vectors after normalization.



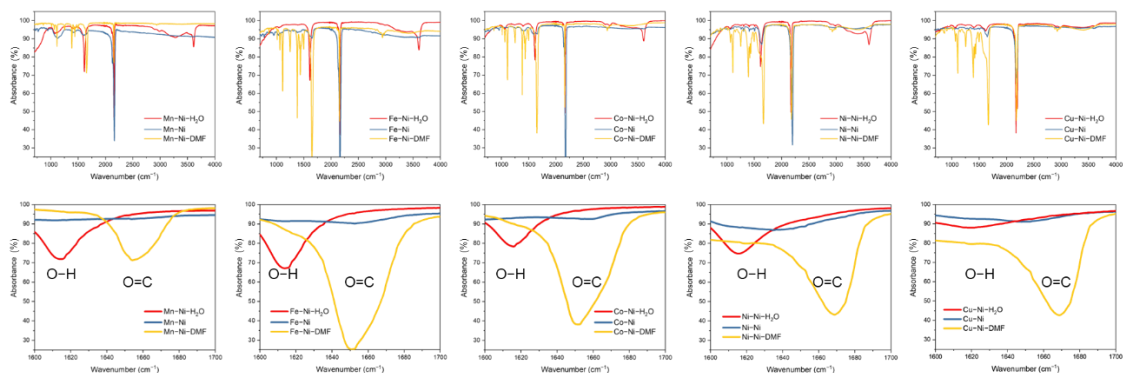
Supplementary Fig. 4 | Feature engineering. Feature engineering to describe different candidates where the dotted boxes indicate feature differences, which are keys to clustering these candidates.



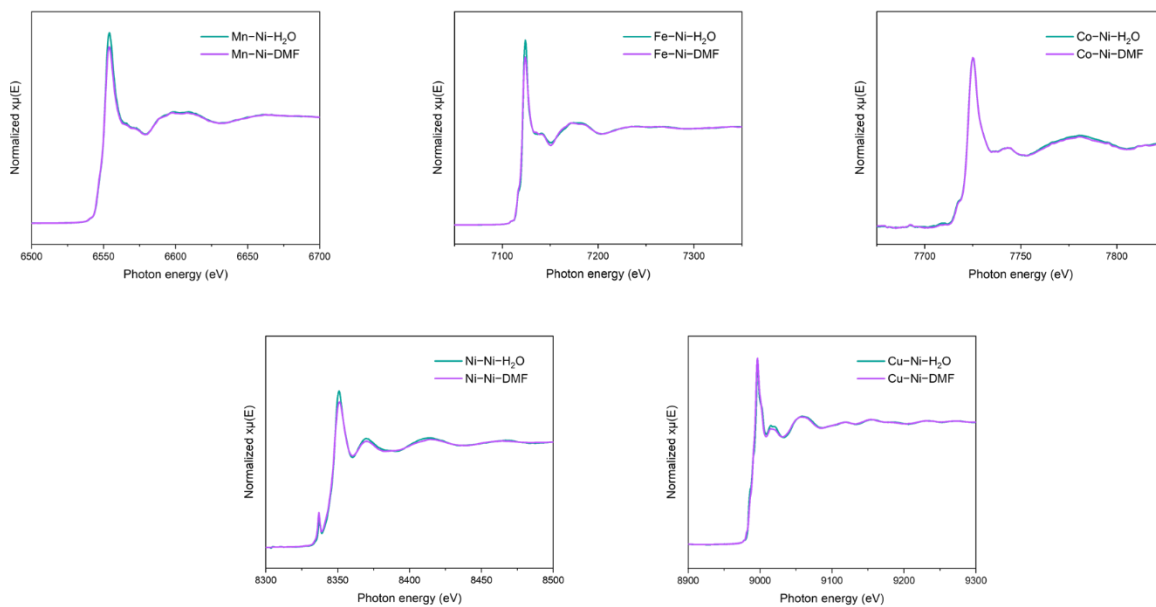
Supplementary Fig. 5 | Geometric configurations of M-Ni-DMF.



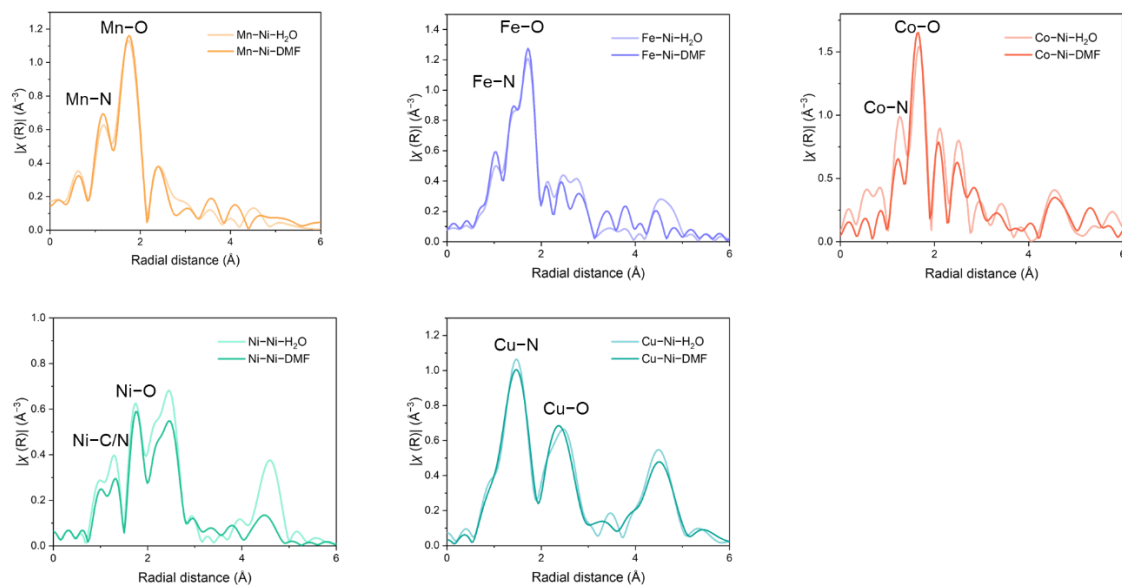
Supplementary Fig. 6 | Scanning electron microscope (SEM) images of M-Ni-DMF (M=Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ or Cu²⁺). Two-dimensional Hofmann complexes M-Ni-DMF where metal centers are linked by organic DMF ligands to create extended two-dimensional networks, featuring a layered structure, as demonstrated in SEM characterization. Series M-Ni-DMFs demonstrated a sheet-like with a similar sheet size of around 1 μm .



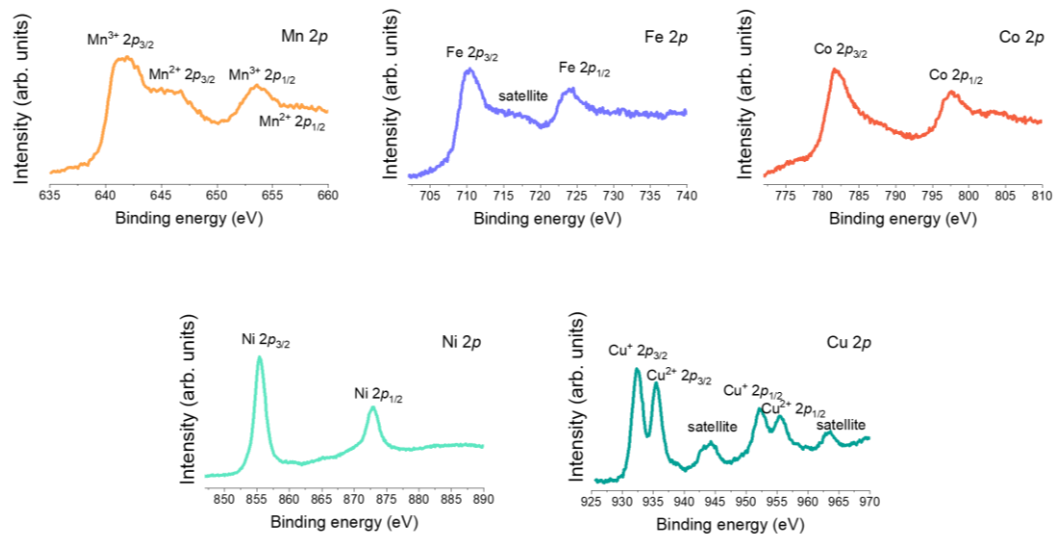
Supplementary Fig. 7 | Fourier transform infrared (FT-IR) spectra of M-Ni-H₂O, M-Ni-activate, and M-Ni-DMF (M=Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ or Cu²⁺). M-Ni-H₂O demonstrated O-H signals which exhibit considerable fading after the heat treatment to exclude the crystal H₂O and most of absorbed H₂O. After the DMF ligands diffusing process, M-Ni-DMF demonstrated prominent C=O signals, suggesting the existence of DMF ligands.



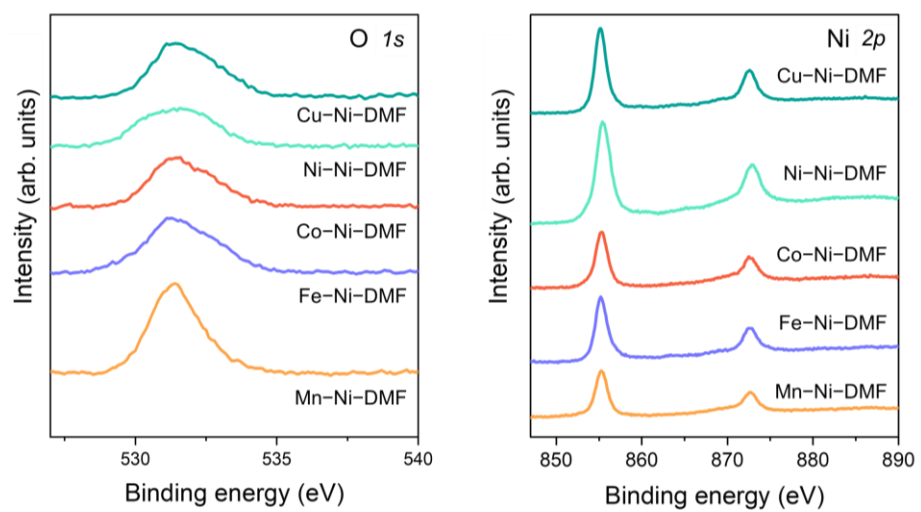
Supplementary Fig. 8 | X-ray absorption near-edge structure analyses of Octahedral metal M K edge of M-Ni-H₂O and M-Ni-DMF (M=Mn²⁺, Fe²⁺, Ni²⁺ or Cu²⁺). The peak shift in the pre-edge and white line range of metal K edge between M-Ni-H₂O and M-Ni-DMF suggests the occurrence of ligand change.



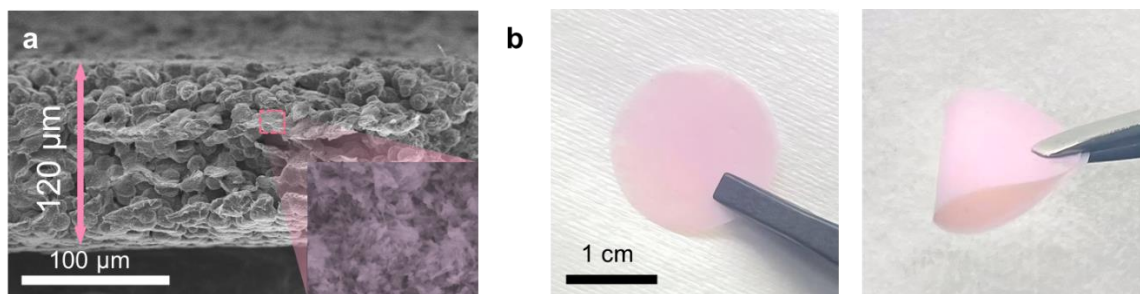
Supplementary Fig. 9 | k^3 -weighted Fourier transform of extended X-ray absorption fine structure (EXAFS) analyses of M-Ni-H₂O and M-Ni-DMF ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}$ or Cu^{2+}). The first coordinated shells are assigned to the M–N scattering paths while the second peak indicates M–O coordination for both M-Ni-H₂O and M-Ni-DMF. The relative peak oscillation of M-Ni-H₂O and M-Ni-DMF reveals the ligand difference.



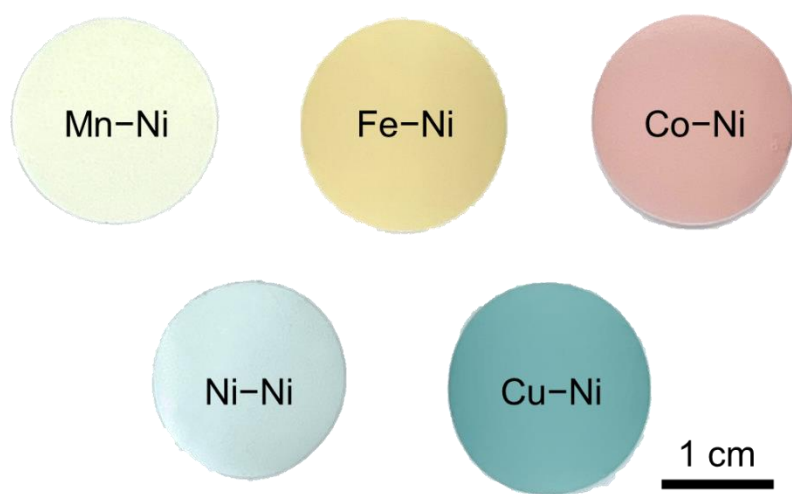
Supplementary Fig. 10 | Mn, Fe, Co, Ni, Cu 2p X-ray photoelectron spectroscopy (XPS) spectra of M-Ni-DMF.



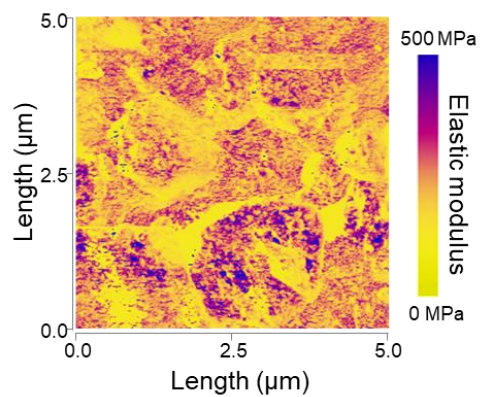
Supplementary Fig. 11 | O 1s and Ni 2p XPS spectra comparison of M-Ni-DMF.



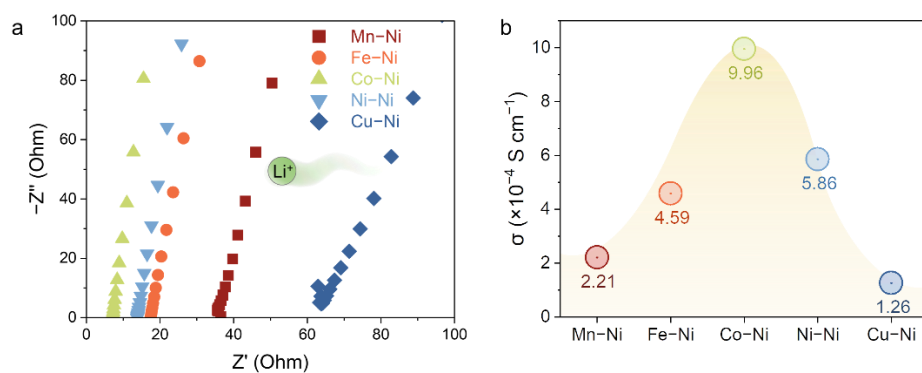
Supplementary Fig. 12 | Co-Ni membrane characterization. **a**, SEM images of Co-Ni membrane. The Co-Ni-DMF nanosheets featured layered morphology, were uniformly dispersed within the PVDF-HFP and LiFSI matrix. **b**, Digital photo of electrolytes exhibiting considerable flexibility. Bending the membrane several times with tweezers demonstrated its good flexibility, as it could return to its original shape without any cracks after multiple bends.



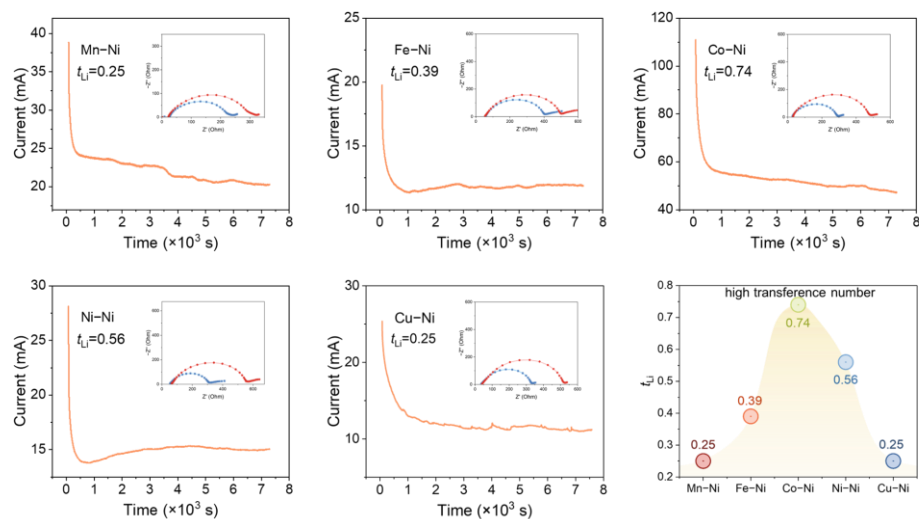
Supplementary Fig. 13 | Digital photos of M–Ni based polymer electrolytes.



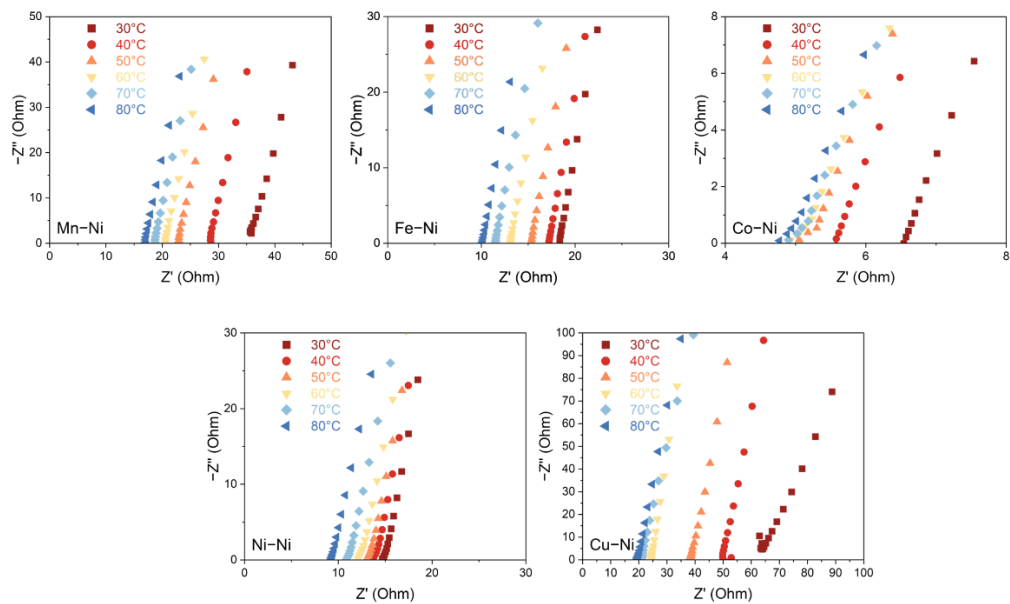
Supplementary Fig. 14 | Elastic modulus distribution map of PVDF-HFP-based membranes probed by atomic force microscopy.



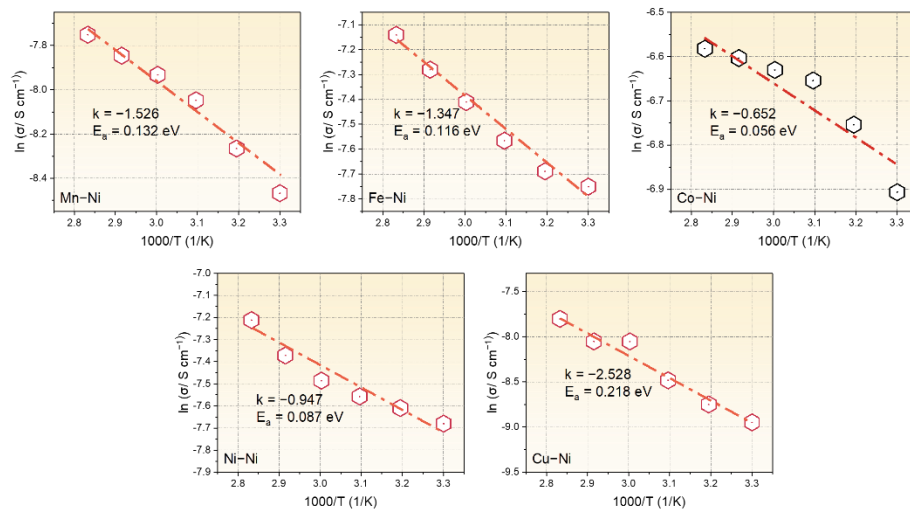
Supplementary Fig. 15 | Ionic conductivity of M-Ni based electrolytes. a, Nyquist plots of electrochemical impedance spectroscopy of M-Ni based electrolytes to calculate **b**, the ionic conductivity according to the equation of $\sigma = L / (R \times S)$ as demonstrated in Methods, testing at room temperature of $30 \text{ }^{\circ}\text{C} \pm 3 \text{ }^{\circ}\text{C}$.



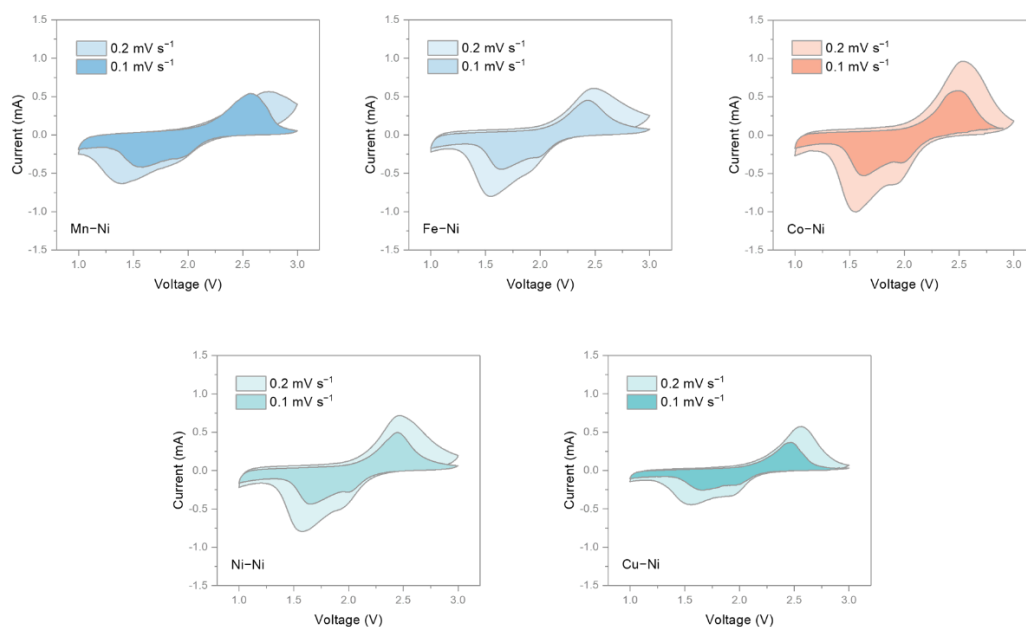
Supplementary Fig. 16 | t_{Li^+} of M-Ni based electrolytes. Steady-state current measurement of the Li||Li symmetric cells under 10 mV polarization to measure the lithium-ion transference number. Inset: Nyquist plots before and after polarization testing at $30\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$.



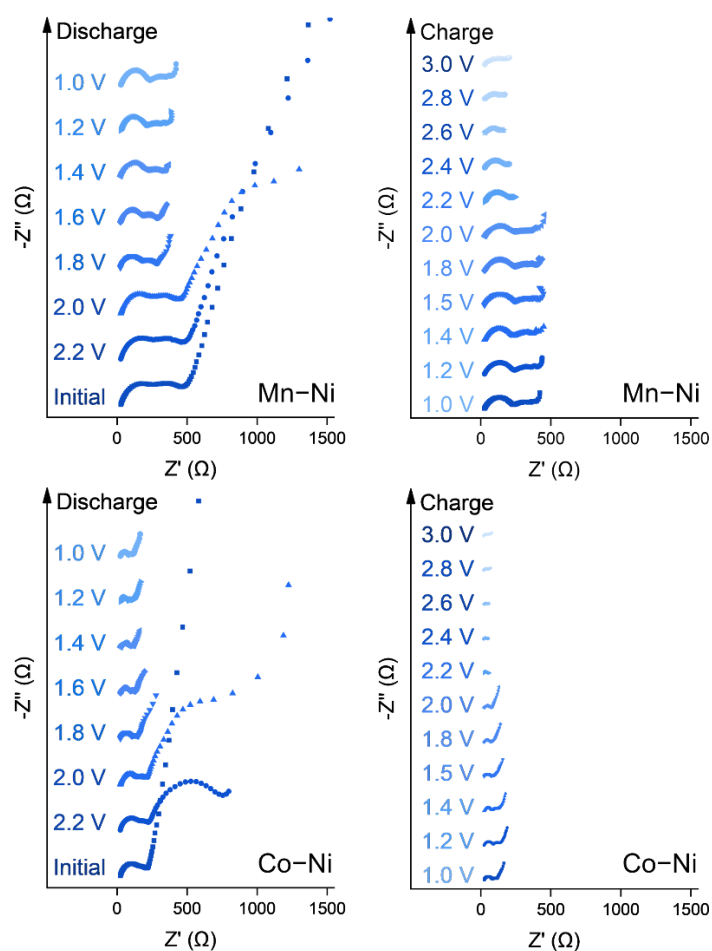
Supplementary Fig. 17 | Typical Nyquist plots measured from 30 °C to 80 °C.



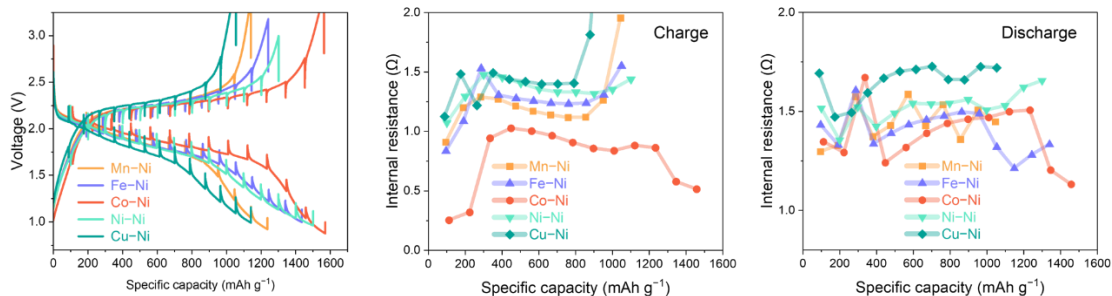
Supplementary Fig. 18 | Arrhenius plots of ionic conductivities of M-Ni based electrolytes.



Supplementary Fig. 19 | Cyclic voltammetry profiles of Li|M-Ni|SPAN cells with different solid-state electrolytes at scanning rates of 0.1 mV s⁻¹ and 0.2 mV s⁻¹.



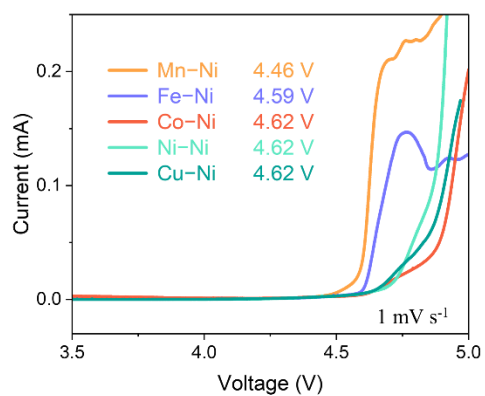
Supplementary Fig. 20 | *In situ* electrochemical impedance spectroscopy profiles of full cells with various electrolytes. *In situ* electrochemical impedance spectroscopy measurements were performed at various stages of charge and discharge for the first cycle at 0.2 C at 30 °C $\pm$ 3 °C.



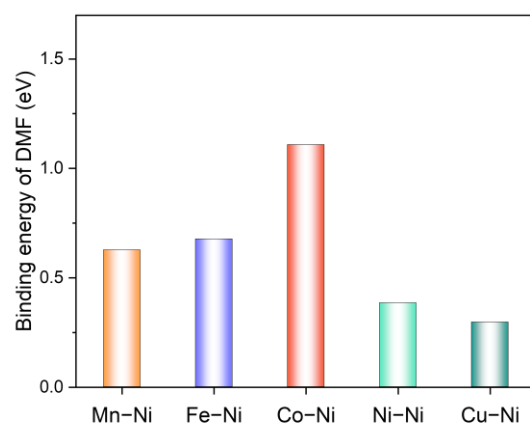
Supplementary Fig. 21 | Galvanostatic intermittent titration measurement. The internal resistance during charge and discharge can be calculated according to the following equation:

$$R_{\text{internal}} = |V_{\text{QOCV}} - V_{\text{CCV}}| / I_{\text{applied}}$$

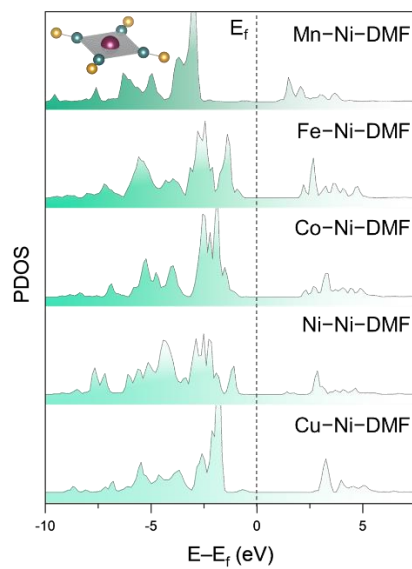
Where R_{internal} is the internal resistance, $|V_{\text{QOCV}} - V_{\text{CCV}}|$ is the voltage difference before and after the pulse of duration, I_{applied} is the applied current ($I_{\text{applied}} = 0.1 \text{ mA}$).



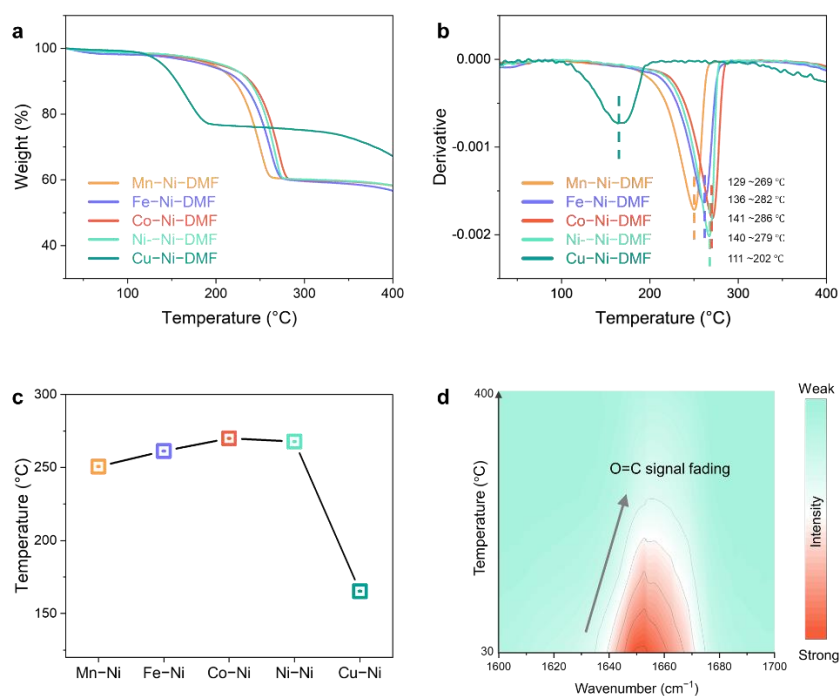
Supplementary Fig. 22 | Linear sweep voltammetry measurements. The electrochemical stability window of electrolytes is estimated by linear sweep voltammetry measurements with a scan rate of 1 mV s⁻¹, where the onset points indicate the oxidation voltage.



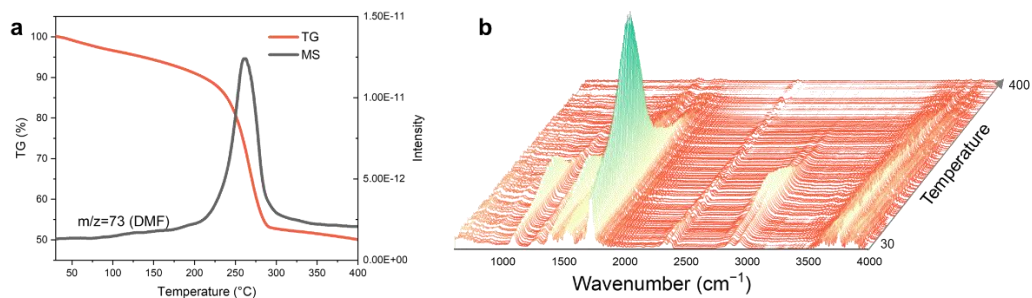
Supplementary Fig. 23 | Binding energy of DMF within the Hofmann complexes.



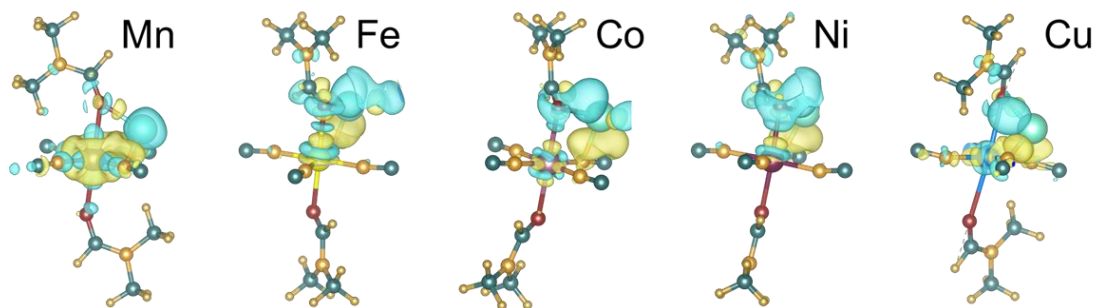
Supplementary Fig. 24 | Projected densities of states (PDOS) of *d* band of square planar Ni sites in M-Ni-DMF. Ni PDOS exhibit varied filling states for different M-Ni-DMF, probably due to the electron transfer from the neighboring atoms in Hofmann frameworks.



Supplementary Fig. 25 | Thermal gravimetric analysis (TGA) curves a, and derivatives b, of M-Ni-DMF detecting the pyrolysis temperature c, and d, escape characteristics of DMF of M-Ni-DMF. *Ex situ* FT-IR spectra of M-Ni-DMF upon the heating process, indicating the escaping behavior of DMF with the signal fading of carbonyl (O=C) peak.

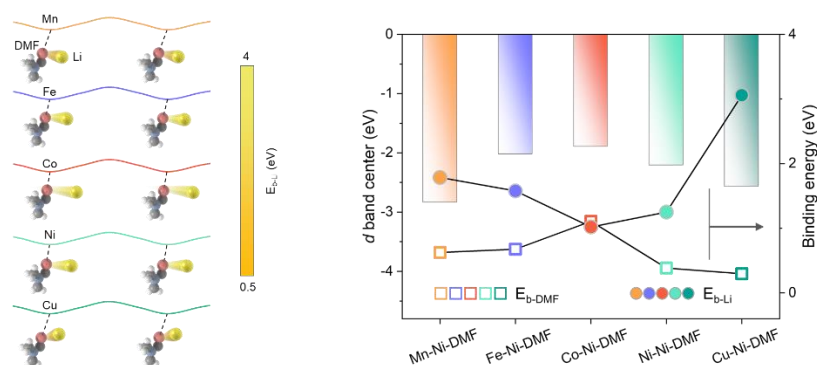


Supplementary Fig. 26 | a, gas chromatography-mass spectra, b, Thermogravimetric analysis-Fourier transform infrared spectra. Thermogravimetric analysis-Fourier transform infrared-gas chromatography-mass spectrometry measurement detecting the product upon the heating process from 30 °C to 400 °C in **Supplementary Fig. 25** which verified the escaping of DMF.



Supplementary Fig. 27 | Charge density difference between M-Ni-DMF surfaces and lithium.

The red, blue, green, yellow, and pale yellow spheres represent oxygen, lithium, carbon, nitrogen, and hydrogen, respectively.



Supplementary Fig. 28 | Binding energy of DMF and Li and their relationships with *d* band center by DFT calculation. The blue, red, grey, white, yellow spheres represent nitrogen, oxygen, carbon, hydrogen, and lithium, respectively. The binding ability to DMF is positively correlated with the *d*-band center of the metal sites but negatively correlated with their binding ability to Li. This is primarily because an elevated *d*-band center enhances the antibonding orbitals of the M-O bond, reducing its occupancy below the Fermi level. Consequently, the integrated crystal orbital Hamilton population (ICOHP) increases, demonstrating a stronger interaction strength with DMF. Meanwhile, lithium exhibits a competitive interaction with the metal for oxygen, where the enhancement of the Co-O bond weakens the Li-O bond, resulting in the weakest lithium coordination ability of Co-Ni-DMF.

Supplementary Table 1 | Summary of 24-dimensional features.

Serial number	Formula mode	Serial number	Formula mode
1	$\lg(\text{abs}(\text{A}(\text{M}_1) + \text{A}(\text{M}_2)))$	13	$\lg(\text{abs}(\text{A}(\text{M}_1) * \text{A}(\text{M}_2)))$
2	$\lg(\text{abs}(\text{Di}(\text{M}_1) + \text{Di}(\text{M}_2)))$	14	$\lg(\text{abs}(\text{Di}(\text{M}_1) * \text{Di}(\text{M}_2)))$
3	$\lg(\text{abs}(\text{Cr}(\text{M}_1) + \text{Cr}(\text{M}_2)))$	15	$\lg(\text{abs}(\text{Cr}(\text{M}_1) * \text{Cr}(\text{M}_2)))$
4	$\lg(\text{abs}(\text{Ep}(\text{M}_1) + \text{Ep}(\text{M}_2)))$	16	$\lg(\text{abs}(\text{Ep}(\text{M}_1) * \text{Ep}(\text{M}_2)))$
5	$\lg(\text{abs}(\text{Gid}(\text{M}_1) + \text{Gid}(\text{M}_2)))$	17	$\lg(\text{abs}(\text{Gid}(\text{M}_1) * \text{Gid}(\text{M}_2)))$
6	$\lg(\text{abs}(\text{Fie}(\text{M}_1) + \text{Fie}(\text{M}_2)))$	18	$\lg(\text{abs}(\text{Fie}(\text{M}_1) * \text{Fie}(\text{M}_2)))$
7	$\text{abs}(\text{A}(\text{M}_1) - \text{A}(\text{M}_2))$	19	$\lg(\text{abs}(\text{A}(\text{M}_1) / \text{A}(\text{M}_2)))$
8	$\text{abs}(\text{Di}(\text{M}_1) - \text{Di}(\text{M}_2))$	20	$\lg(\text{abs}(\text{Di}(\text{M}_1) / \text{Di}(\text{M}_2)))$
9	$\text{abs}(\text{Cr}(\text{M}_1) - \text{Cr}(\text{M}_2))$	21	$\lg(\text{abs}(\text{Cr}(\text{M}_1) / \text{Cr}(\text{M}_2)))$
10	$\text{abs}(\text{Ep}(\text{M}_1) - \text{Ep}(\text{M}_2))$	22	$\lg(\text{abs}(\text{Ep}(\text{M}_1) / \text{Ep}(\text{M}_2)))$
11	$\text{abs}(\text{Gid}(\text{M}_1) - \text{Gid}(\text{M}_2))$	23	$\lg(\text{abs}(\text{Gid}(\text{M}_1) / \text{Gid}(\text{M}_2)))$
12	$\text{abs}(\text{Fie}(\text{M}_1) - \text{Fie}(\text{M}_2))$	24	$\lg(\text{abs}(\text{Fie}(\text{M}_1) / \text{Fie}(\text{M}_2)))$

Where A(), Di(), Cr(), Ep(), Gid() and Fie() represent atomic number, dipole polarizability, covalent radius, Pauling energy, group_id, and first ionization energy respectively. M₁, and M₂ represent two metal sites, abs() represents the absolute value, lg() represents the logarithm.

Supplementary Table 2 | Summary of sulfur-based solid-state and quasi-solid-state batteries reported in the literature.

Electrolytes	Initial Specific capacity (mAh g ⁻¹)	Specific capacity after cycling (mAh g ⁻¹)	Rate (C)	Cycle	Decay (%)	Ref
Co-Ni	1275.2	829.6	0.2	500	0.07	This work
	1076.9	964	0.5	200	0.05	
PEO-LGPS	~1380	588	0.1	50	1.15	1
PEO-PAN	1110	380	/	100	0.66	2
PEO/PVDF-LiTFSI	818	630	0.1	60	0.38	3
poly(DOL)/PEG-SiO ₂	1100	500	0.1	110	0.50	4
Quasi DOL	750	450	1166 mA g ⁻¹	500	0.08	5
Li ₃ PS ₄	552.6	410.5	0.2	100	0.25	6
SeS ₂ -Li ₃ PS ₄	1024	935	0.4 A g ⁻¹ .	100	0.09	7
Li ₆ PS ₅ Cl	1270	1066.8	0.1	100	0.16	8
LPC@2%UCPBA	~900	720	0.5	180	0.44	9
PVDF-HFP	1325	897.4	0.2	100	0.32	10
SSP/PDOL	1110	717	0.2	200	0.18	11
PTMG-HDI-BHDS	962	812	0.3	350	0.05	12
S _{9.3} I/LGPS	794.6	701	0.16 A g ⁻¹	400	0.03	13

Supplementary References

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