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Ni^{II} and Cu^{II} coordination polymers as anode materials and their compatibility with different electrolytes in Li-ion batteries

Guzaliya R. Baymuratova, Ekaterina A. Komissarova, Galiya Z. Tulibaeva, Olga V. Yarmolenko, Olga A. Kraevaya and Pavel A. Troshin

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Experimental section

1.1. Materials and methods

MOF, Timcal Super C65 (MTI) carbon black and polyvinylidene difluoride (PVDF) HSV 900 (KynarFlex) polymer binder were used as cathode components. Prototypes of Li//**P1**(**P2**) batteries and **P1**//**P1** (**P2**//**P2**) cells of the CR2032 coin type were assembled in an MBraun argon glove box (Germany) for use with the BTS 5V10mA test system (Shenzhen Neware Electronic Co., LTD, China) in galvanostatic mode at different current values. Impedance measurements were carried out in symmetrical **P1**//**P1** (**P2**//**P2**) cells using a Z-2000 impedance meter (Elins, Russia) in the frequency range from 1 Hz to 500 kHz at a signal amplitude of 10 mV. The measurement results were processed using the ZView2 program with an average error in determining the parameters of the equivalent circuit elements of 10%.

Cyclic voltammetry (CV) curves of Li//**P1**(**P2**) cells were recorded on a P-40X potentiostat-galvanostat (Elins, Russia) at a scan rate of 1 mV s^{-1}.

Electrical conductivity was measured on a P-8 potentiostat (Elins, Russia). The shape of the dependence of the current I on the voltage U was removed, and the sweep rate was 2 mV s^{-1}. Cell resistance was calculated according to Ohm's law:

$$R = U / I, \tag{S1}$$

where U is voltage (V), I is current (A) and R is resistance (Ohm).

The electronic conductivity was calculated by the formula:

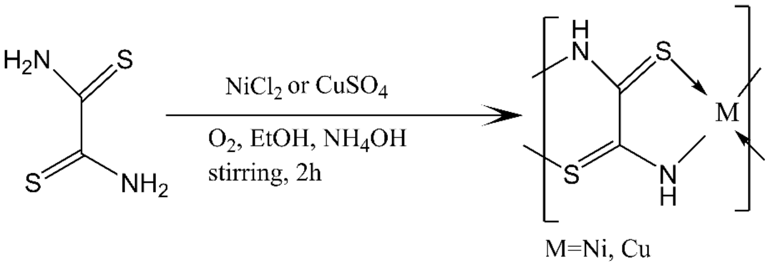
$$\sigma = d / (R\, S), \tag{S2}$$

where d is the sample thickness and S is the electrode surface area ($S = 0.2\ \text{cm}^2$).

Using a FRITSCH Analysette 22 NanoTec laser particle sizer, the particle sizes of **P1** and **P2** were determined in the range of 0.01–2000 μm with sonication.

1.2. Synthesis of MOF

The method for obtaining **P1** and **P2** is described in detail in the cited work.[S1]



Scheme S1 Synthesis of MOFs **P1** and **P2**.

1.3. Li-ion battery fabrication and testing

Cathode composition: MOF/carbon black/PVDF = 50 : 40 :10 (w/w). A solution of PVDF in *N*-methylpyrrolidone (NMP) was prepared in a weighing cup. For this, 0.1 g of cathode material was taken per 1.5 ml of solvent. The mixture was stirred with a magnetic stirrer at 50 °C for 24 h. Then the cathode mass was spread over an aluminum support (d = 20 μm) using a Doctor Blade tool and dried at 150 °C for 4 h to remove the solvent (visually assessed). Then the cathodes were roll pressed. The pressed cathodes were dried in a drying box at 120 °C for 10 h until the residual NMP solvent was completely removed. The MOF load was about 0.56 mg cm^{-2}.

Prototypes of lithium–organic batteries were tested using three types of electrolytes: (1) 1 M LiTFSI solution in 1,3-dioxolane–1,2-dimethoxyethane (DOL–DME, 2 : 1, v/v), (2) 1 M LiTFSI in tetraglyme and (3) a mixture of 1 M LiTFSI in DOL–DME and 1 M $LiPF_6$ in ethylene carbonate–dimethyl carbonate (1 : 1, v/v). The charge/discharge current was calculated from the theoretical value of the specific capacitance, taking into account the MOF mass on the electrode. Thus, C_{theor} (**P1**) = 303 mA h g^{-1} and C_{theor} (**P2**) = 295 mA h g^{-1} are the theoretical capacitances for the 2-electron transition.

1.4. Quantum chemical modeling

Quantum chemical modeling of the structure of coordination polymers **P1** and **P2**, as well as their interaction with lithium, was carried out by the Perdew–Burke–Ernzerhof (PBE) density functional method[S2] using the Stevens–Bash–Krauss (SBK) pseudopotential[S3] and the extended basis: C, N, O [10*s*, 7*p*, 3*d*/3*s*, 2*p*, 1*d*], Li [10*s*, 7*p*, 3*d*/4*s*, 3*p*, 1*d*] and H [6*s*, 2*p*/2*s*, 1*p*]. The Hirschfeld method was used to calculate atomic charges.

References

S1 E. A. Komissarova, O. A. Kraevaya, I. S. Zhidkov, A. I. Kukharenko, N. N. Dremova, Y. V. Baskakova, A. F. Shestakov and P. A. Troshin, *Synth. Met.*, 2023, **293**, 117300.

S2 P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

S3 W. J. Stevens, H. Basch and M. J. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026.

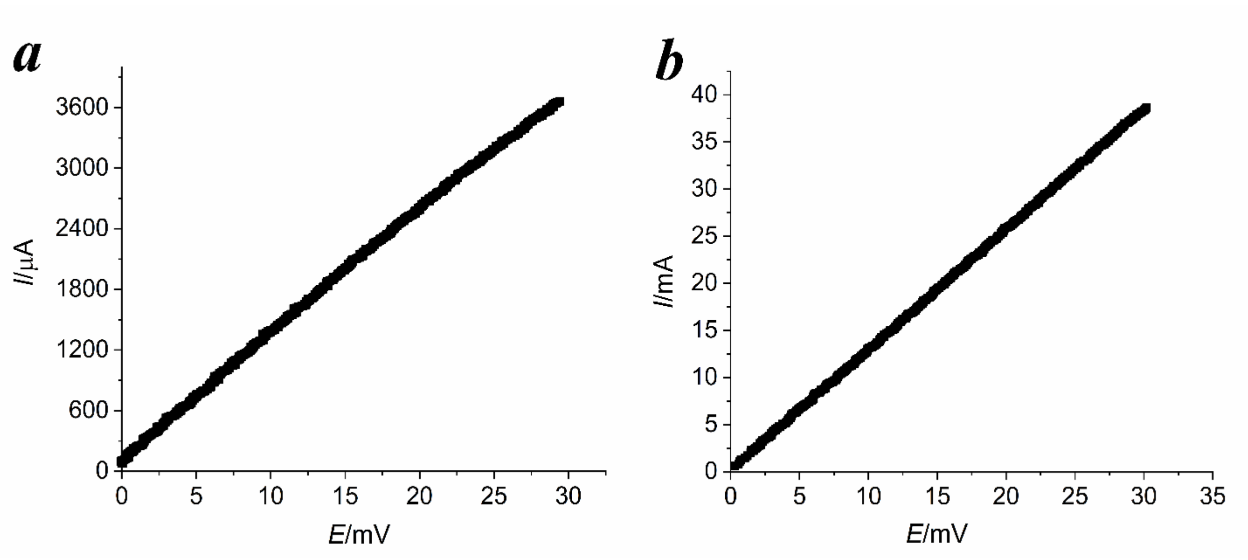


Figure S1 Current–voltage characteristics of (*a*) **P1** and (*b*) **P2.**

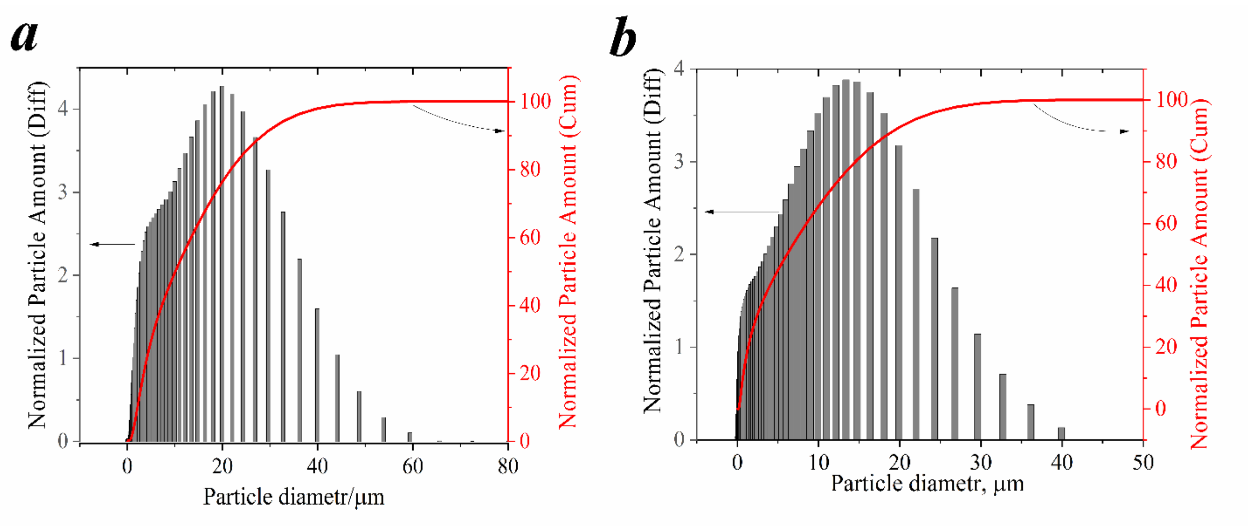
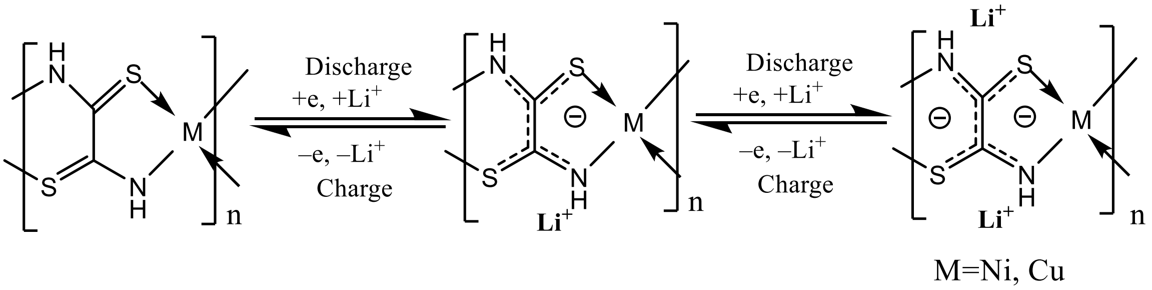


Figure S2 Particle size distributions of (*a*) **P1** and (*b*) **P2**.



Scheme S2 Redox transformation of MOF.

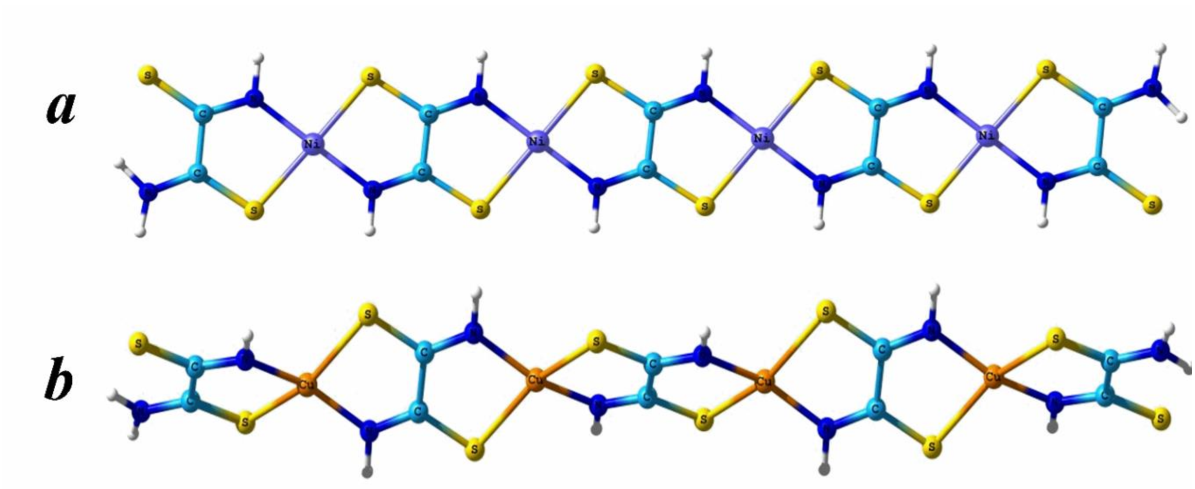


Figure S3 Quantum chemical models of coordination polymers (*a*) **P1** and (*b*) **P2**.

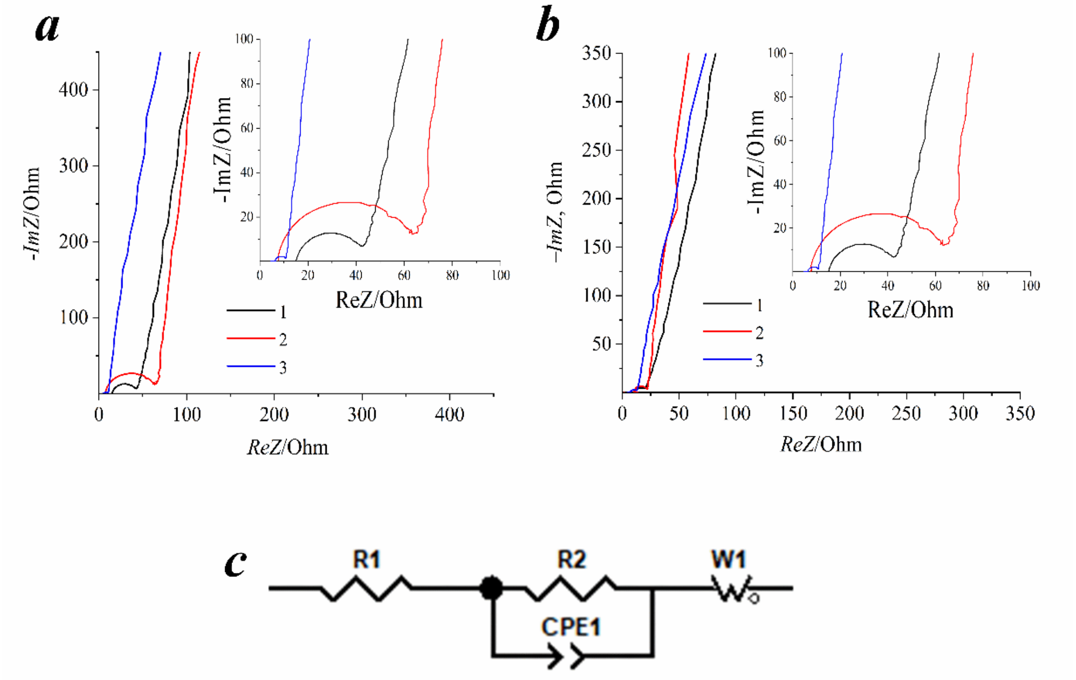


Figure S4 Nyquist plots for (*a*) **P1**//**P1** and (*b*) **P2**//**P2** cells with electrolytes consisting of (*1*) 1 M LiTFSI in DOL–DME (2 : 1, v/v.), (*2*) 1 M LiTFSI in tetraglyme and (*3*) a mixture of 1 M LiTFSI in DOL–DME (2 : 1, v/v.) and 1 M $LiPF_6$ in EC–DMC (1 : 1, v/v), as well as (*c*) equivalent circuit models, where *R*1 is the electrolyte resistance, *R*2 is the electrode/electrolyte interface resistance, *CPE*1 is the constant phase element, and *W*1 is the open Warburg impedance.

Table S1 Calculated parameters of equivalent cell circuits**.**

Cells	**P1**//**P1**			**P2**//**P2**		
Electrolyte no.	1	2	3	1	2	3
*R*1/Ω	15	7	6	10	8	6
*R*2/Ω	45	60	3.86	6.6	12.7	9.09
*CPE*1-*T*/F	2.7×10^{-6}	2.9×10^{-6}	2.34×10^{-6}	7.7×10^{-6}	2.0×10^{-6}	3.8×10^{-6}
*CPE*1-*P*	0.98	0.99	0.99	0.9	0.92	0.90
*W*1-*R*/Ω	39.1	41	5.2	21.5	6.9	5.3
*W*1-*T*/s	0.0098	0.0049	0.0002	0.0009	0.0002	0.0005
*W*1-*P*	0.46	0.46	0.46	0.43	0.47	0.46

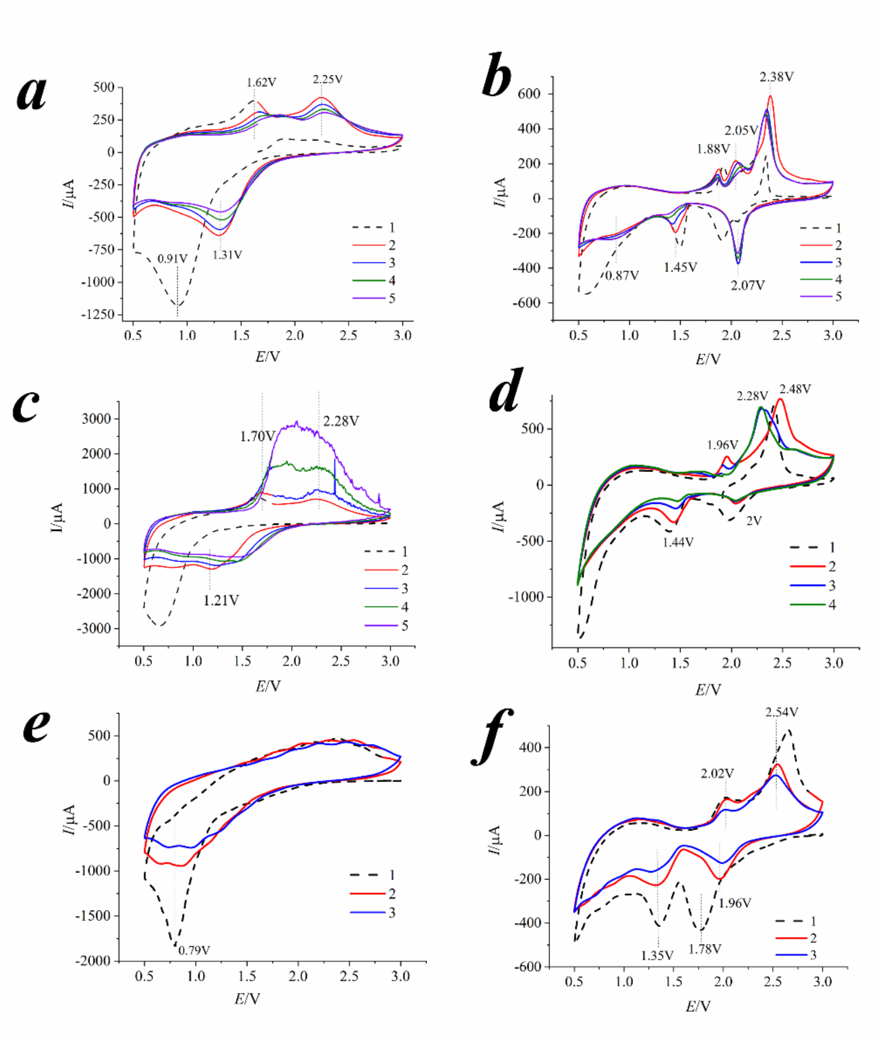


Figure S5 CV profiles of (*a*),(*c*),(*e*) Li//**P1** and (*b*),(*d*),(*f*) Li// **P2** cells over a potential range of 0.5–3.0 V at a scan rate of 1 mV s^{-1} in electrolytes (*a*),(*b*) no. 1, (*c*),(*d*) no. 2 and (*e*),(*f*) no. 3.

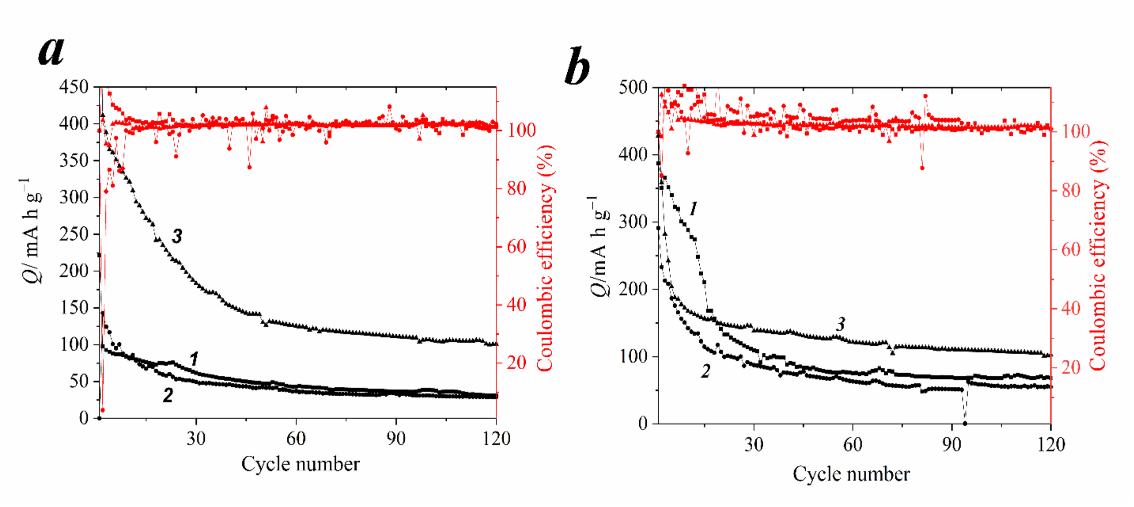


Figure S6 Dependence of the specific capacitance and Coulombic efficiency of Li//**P1** (*a*) and Li//**P2** cells (*b*) on the number of cycles in the voltage range of 0.5–3.0 V at a current density of 0.15 A g^{-1} using electrolytes consisting of (*1*) 1 M LiTFSI in DOL–DME (2 : 1, v/v.), (*2*) 1 M LiTFSI in tetraglyme and (*3*) a mixture of 1 M LiTFSI in DOL–DME (2 : 1, v/v.) and 1 M LiPF$_6$ in EC–DMC (1 : 1, v/v).