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Metal complexes of folic acid for lithium ion storage

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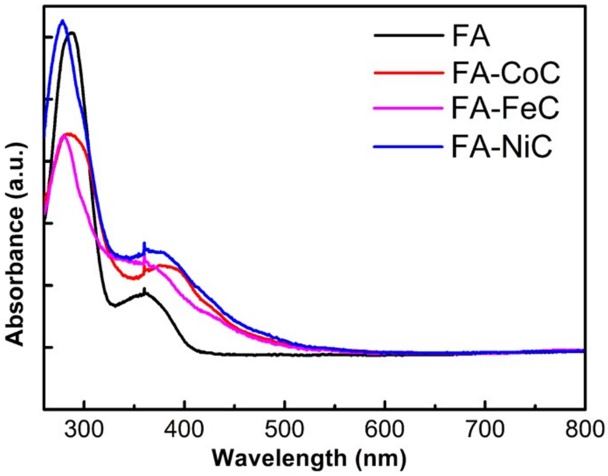
1. Experimental section

1.1 Synthesis of materials: For a typical synthesis of FA-CoC, Folic acid (0.4414 g, 1.0 mmol) was added into 10 mL ethanol with stirring for 1 h at room temperature to form a yellow transparent solution. Then $CoCl_2 \cdot 6\ H_2O$ (0.237 g, 1.0 mmol) was dissolved into the solution under vigorous stirring. After refluxing at 80 ^oC for 24 h, the black sediment was collected, washed with water, ethanol for several times, and dried at 60 ^oC under vacuum. Similarly, when the cobalt salt was replaced by $FeCl_3 \cdot 6\ H_2O$ (0.270 g, 1.0 mmol) or $NiCl_2 \cdot 6\ H_2O$ (0.238 g, 1.0 mmol), the obtained products were denoted as FA-FeC and FA-NiC respectively.

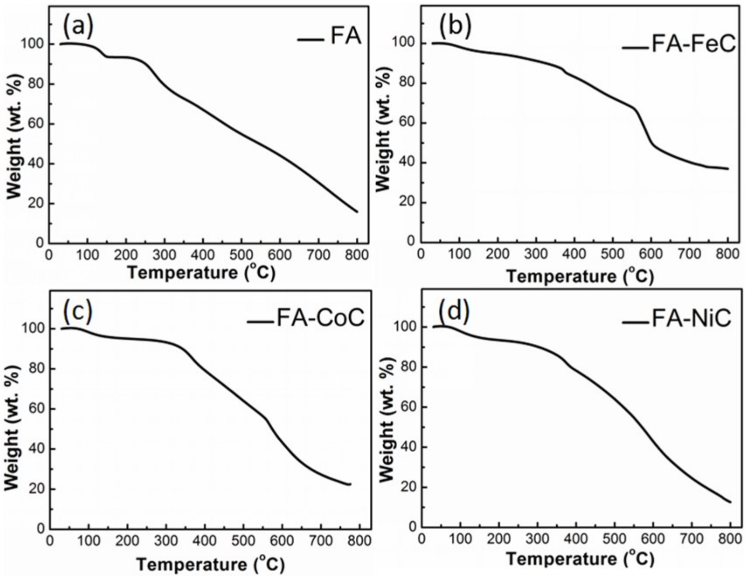
1.2 Electrochemical measurements: For the working electrodes, a certain amount of folic acid-metal complexes, conducting carbon (Super P carbon black from Alfa aesa) and binder (Polytetrafluoroethylene, PTFE) were mixed with a mass ratio of 6.5:3:0.5 by a pestle and mortar followed by pressing on a current collector (copper foil). A coin-type half cell (CR2032) configuration was assembled in argon-filled glove box, in which lithium metals and Celgard membranes (2502) was used as reference electrodes and separators, respectively. A mixture of 1 M LiPF6, ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, volume ratio) were used as the electrolyte. The galvanostatic charge and discharge experiments were implemented on a NEWARE battery testing system in the potential range from 0.01 to 3 V. Cyclic voltammetry (CV) were recorded on an electrochemical work station (CHI 630D) in the voltage range 0–3V at a scanning rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out on a PARSTAT 2273 electrochemical work station in the frequency range from 100 kHz to 10 mHz with an AC amplitude of 5 mV.

1.3 Materials characterization: Fourier transform infrared spectroscopy (FTIR) was measured on Thermo Nicolet (Nicolet 5700) in the wavenumber range of 3800-500 cm^{-1}. The thermogravimetric analysis (TGA) was carried out on Perkin Elmer Diamond TGA4000 apparatus with a heating rate of 10 ^oC min^{-1} from 30 ^oC to 800 ^oC

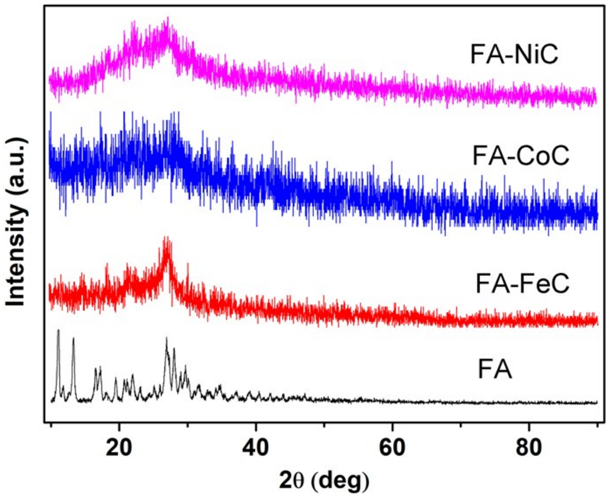
under a flowing N_2. The X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250 (Thermo Electron). The X-ray excitation was provided by a monochromatic Al Kα (1486.6 eV) source. Survey scans were obtained using a passing energy of 100 eV while high resolution scans of specific elements were obtained using a 20 eV pass energy. The detection of the emitted photoelectrons was performed perpendicularly to the surface sample. Data quantification was performed on the Avantage program. The surface atomic concentrations were determined from photoelectron peaks areas using the atomic sensitivity factors reported by Scofield. Binding energies (BE) of all core levels were referred to the C−C bond of C1s at 284.6 eV. Ultraviolet−visible (UV−vis) spectra were recorded on an Agilent 8453 UV−vis spectrophotometer. The ICP-MS measurements were performed with an Agilent 7700x Series ICP-MS (Agilent Technologies).



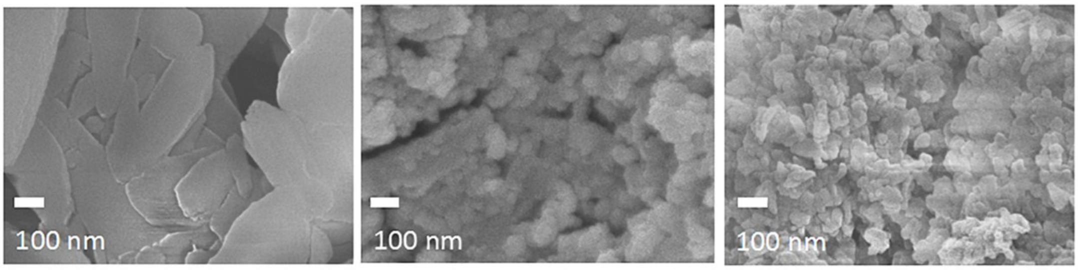
2. Fig. S1 UV−vis spectra of FA and FA-MCs.



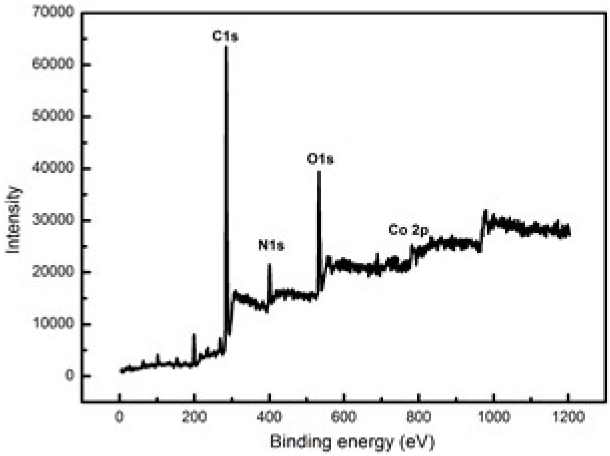
3. Fig. S2 TGA curves of (a) FA, (b) FA-FeC, (c) FA-CoC and (d) FA-NiC.



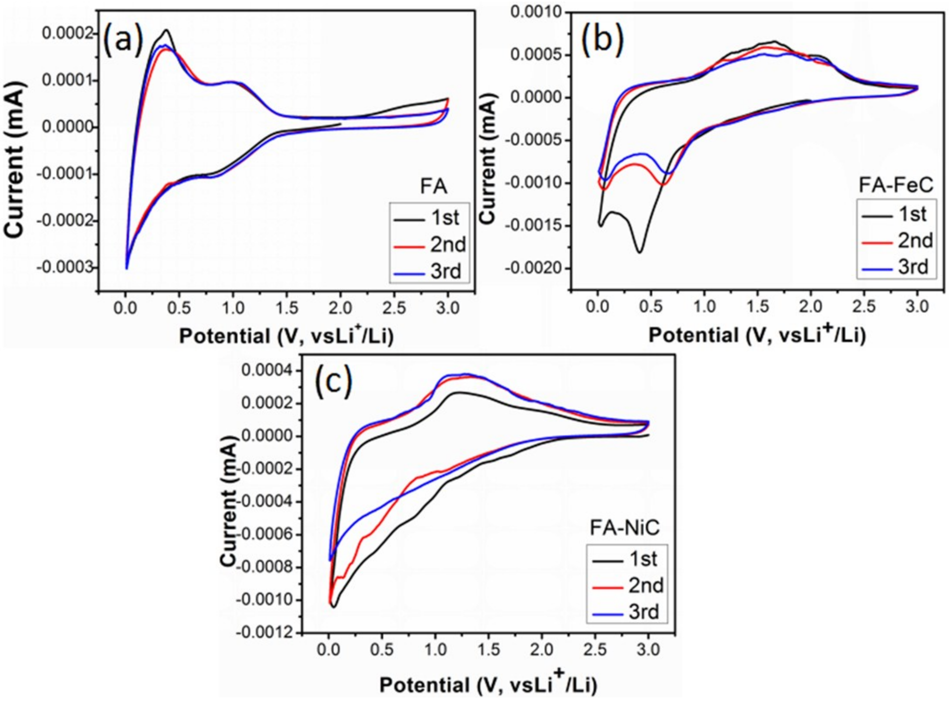
4. Fig. S3 XRD patterns of FA and FA-MCs.



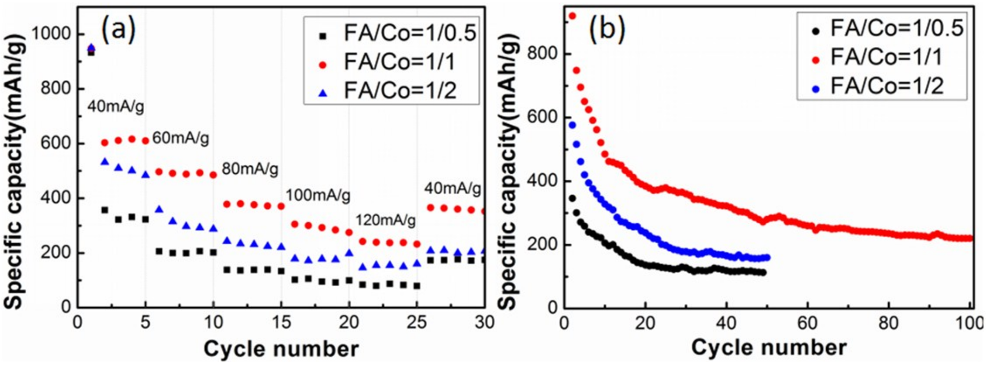
5. Fig. S4 SEM images of (a) FA, (b) FA-FeC and (c) FA-NiC.



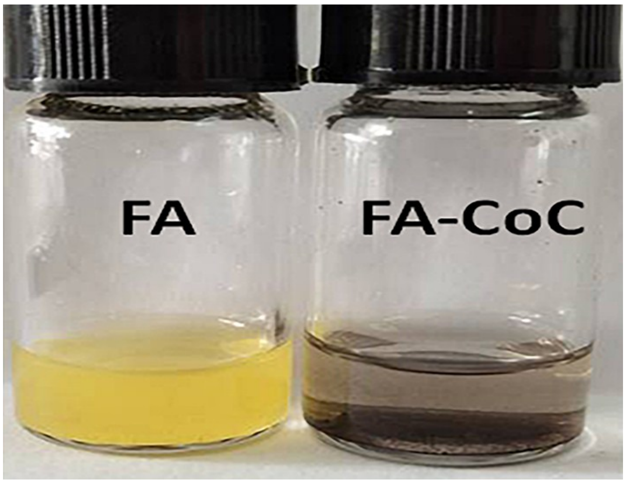
6. Fig. S5 XPS survey scan of FA-CoC.



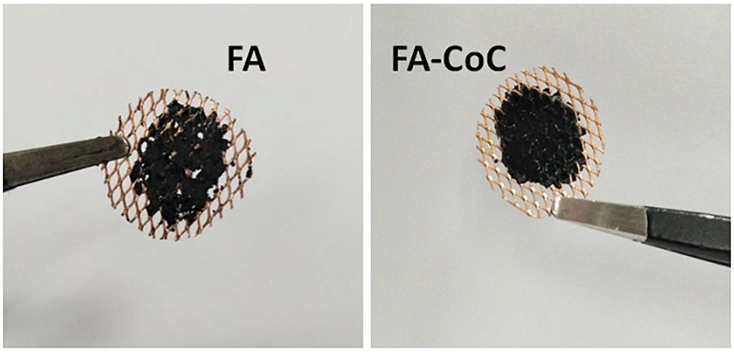
7. Fig. S6 CV curves of (a) FA, (b) FA-FeC, and (c) FA-NiC between 0 and 3V at a scan rate of 0.1 mV s^{-1}.



8. Fig. S7 (a) rate performance of different content of Co^{2+} in FA-CoC at various current densities; (b) Comparison of cycling performance of different content of Co^{2+} in FA-CoC.



9. Fig. S8 Dissolving behaviours of FA (left) and FA-CoC (right) in electrolytes.



10. Fig. S9 Optical images of FA (left) and FA-CoC (right) electrodes (after cycling 20 times).(Note that, after cycling 20 times, the cobalt content in electrolyte is $8.3*10^{-6}$ mol L^{-1}, which is close to the data before cycling $7.8*10^{-6}$ mol L^{-1} (Detected by ICP-MS analysis)).

11. Table S1 the metal content in FA-MCs

Sample Name	**Metal content**	**The molar ratio of metal ions to folic acid**
FA-FeC	21.4%	1:2.1
FA-CoC	21.9%	1:2.1
FA-NiC	22.7%	1;2.2

12**. Table S2** possible storage mechanisms of FA.

$C=O + Li^+ + e^- \leftrightarrow C\text{-}OLi$
$O=C\text{-}O + 2Li^+ + 2e^- \leftrightarrow LiO\text{-}C\text{-}OLi$
$C=N + Li^+ + e^- \leftrightarrow C\text{-}NLi$

13. **Table S3** Impedance values acquired from fitted EIS plots. (the ohmic resistance (R_s), the SEI film resistance (R_{SEI}), the charge transfer resistance (R_{ct}) and the Warburg impedance (Z_w))

Sample	Rs (Ω)	C_{SEI}	R_{SEI} (Ω)	C_{dl}	R_{ct} (Ω)	Z_W(Ω•cm^{-2})
FA	11.4	2.648E-6	94.5	4.9654E-7	210.4	309
FA-FeC	15.37	7.5675E-6	68.9	1.5733E-6	147.6	193.9
FA-CoC	9.9	5.7088E-6	34.45	6.4916E-7	61.54	57.14
FA-NiC	12.29	5.7796E-6	38.95	1.1497E-6	74.56	85.84

14. Table S4 The quantitative residual quantity of FA during the dissolution progress.

Sample	**Initial mass (g)**	**Electrolyte (mL)**	**Residual mass (g)**
FA	0.03	3	0.02
FA-CoC	0.03	3	0.028