Reformation of organic dicarboxylate electrode materials for rechargeable batteries by molecular self-assembly

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Supplementary Information

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Experimental procedure.

Synthesis of 2,6-Naphthalene dicarboxylate dilithium (2,6–Naph(COOLi)₂)

2,6-naphthalene dicarboxylate dilithium (2,6-Naph(COOLi)₂) was synthesized under reflux conditions in methanol by using lithium hydroxide monohydrate (LiOH·H₂O), 2,6-naphthalenedicarboxylic acid (2,6-Naph(COOH)₂), and methanol as starting materials. 0.556 g LiOH·H₂O was dissolved in 100 mL methanol, and 1.0 g 2,6-Naph(COOH)₂ was rapidly added to the methanol solution at room temperature with stirring. The solution initially remained clear, with a white precipitate forming over the course of 30 min. The obtained suspension was stirred under reflux conditions for 12 h. The solid obtained after stirring was filtered, washed with methanol, and dried under vacuum at 393 K; the product was obtained as needle-shaped crystals (90% yield, based on the amount of Li used). The powder of 2,6-Naph(COOLi)₂ was annealed at temperatures between 523 and 723 K for 12 h under Ar atmosphere in a quartz vessel. After annealing, the product was obtained as a white or gray powder (yield 100%).

Characterization data

Thermogravimetric (TG) analysis.

TG analyses were conducted in an Ar atmosphere using a TG-DSC System Thermo Plus EVO II (Rigaku) with a heating rate of 2 K/min to a maximum temperature of 1023 K.

Scanning electron microscope (SEM).

SEM measurements were conducted on 2,6-Naph(COOLi)₂ powder before and after heat treatment using VHX-D510 (KEYENCE). All images were measured in insulation mode.

X-Ray powder diffraction.

The X-ray diffraction patterns were obtained using a Rigaku Smartlab diffractometer with Cu K α radiation at 45 kV and 200 mA in the range $2\theta_{CuK\alpha} = 2-70^{\circ}$ with a step size of 0.01°, scan size per minute of 0.1°. The data were recorded in transmission mode using a foil sample holder. X-Ray data sets were refined by conventional Rietveld methods using the GSAS package and EXPGUI interface.¹ Background, scale factor, zero point, lattice parameters, atomic positions, and the coefficient of the peak shape function were iteratively refined until convergence was achieved.

Electrochemical measurements.

The electrochemical properties of 2,6-Naph(COOLi)₂ were examined using coin-type cells assembled in an Ar-filled glovebox. 2,6-Naph(COOLi)₂-based working electrodes were prepared by coating a dispersion composed of 77.7 wt% 2,6-Naph(COOLi)₂, 13.7 wt% carbon black (as a conducting agent), 5.5 wt% carboxy methyl cellulose, and 3.2 wt% styrene butadiene rubber (as a binder) in distilled water on copper foil. Typically, ca. 4 mg cm⁻² of the powdered mixture was used per cell. These electrodes were dried at 120°C under vacuum for at least 10 h before construction of the electrochemical cell. Li metal was used as the counter electrode, and a microporous polypropylene film as a separator. 1 M LiPF₆ dissolved in a solution of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (30:40:30 volume ratio, respectively) was used as the electrolyte. Galvanostatic charge-discharge tests of 10 cycles with 2,6-Naph(COOLi)₂/Li cells were conducted at 298 K between 0.5 and 1.5 V vs. Li/Li⁺ at a rate corresponding to fully charging to the theoretical capacity of the 2,6-Naph(COOLi)₂ per 10 h (C/10 rate).



Fig. S1 TG analysis of 2,6-Naph(COOLi)₂ after heat treatment. Lithiation of 2,6-Naph(COOH)₂ resulted in a higher temperature for the weight drop. Heat treatment did not affect the starting temperature of the weight drop.



Fig. S2 SEM images of 2,6-Naph(COOLi)₂ powders obtained by heat treatment.



Fig. S3 Charge-discharge curves for Li/2,6-Naph(COOLi)₂ cells. Galvanostatic charge-discharge tests of 10 cycles for Li/2,6-Naph(COOLi)₂ cells were conducted at 298 K between 0.5 and 1.5 V vs. Li/Li⁺ at a rate corresponding to fully charging the theoretical capacity of the 2,6-Naph(COOLi)₂ per 10 h (C/10 rate). The major factor of the initial irreversible capacity is attributed to reductive decomposition of electrolyte.²



Fig. S4 Discharge capacities and coulombic efficiency *vs.* cycle number with varying rates for a Li/2,6-Naph(COOLi)₂ cell using pristine 2,6-Naph(COOLi)₂ and samples annealed at various temperatures.



Fig. S5 Rietveld refinement of X-ray diffraction patterns of pristine and annealed samples.

	Pristine	523 K	573 K	623 K	673 K	723 K
Cell setting	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c					
a/Å	10.2992(9)	10.2880(8)	10.2722(2)	10.2762(2)	10.2699(2)	10.2714(2)
b/Å	5.332(6)	5.3317(5)	5.3430(1)	5.3457(1)	5.3420(1)	5.3432(1)
c/Å	8.6584(9)	8.6485(7)	8.6306(2)	8.6364(2)	8.6311(1)	8.6325(2)
β/°	98.203(4)	98.317(4)	98.830(9)	98.841(9)	98.862(9)	98.871(9)
V/Å ³	470.6(1)	469.4(1)	468.07(2)	468.8(2)	467.87(2)	468.10(2)
Density/g cm ⁻³	1.609	1.614	1.618	1.616	1.619	1.618
R_{wp}	0.1787	0.1366	0.0573	0.0569	0.0489	0.0428
R _p	0.0986	0.0762	0.0392	0.0385	0.0323	0.0277

 Table S1 The results of the crystallographic data obtained from Rietveld refinement.

References

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