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Nickel tetrathiooxalate as a cathode material for potassium batteries

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Experimental section

Synthesis of 1,3,4,6-tetrathiapentalene-2,5-dione: 1,3,4,6-Tetrathiapentalene-2,5-dione was prepared in the reaction of mercury(II) acetate with 1,3,4,6-tetrathiapentalene-5-thiooxo-2-one,[1] which was synthesized by treating the bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate with phosgene in acetone solution.[1] Bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate, in its turn, was prepared as reported by G. Stemecke *et al*.[2]

Synthesis of NiTTO: Metallic sodium (16.3 mmol, 376 mg) was dissolved in 60 mL of absolute ethanol in an argon atmosphere at 0 °C. 1,3,4,6-Tetrathiapentalene-2,5-dione (3.52 mmol, 733.8 mg) was added in argon flow to the resulting solution, and the mixture was refluxed in Ar for 14 h. After cooling, $NiCl_2$ (3.52 mmol, 456.6 mg) was added in Ar flow, and the mixture was heated at reflux in Ar for another 12 h. Afterward, the mixture was cooled and stirred in the air overnight. The precipitate was filtered, thoroughly washed with ethanol and water, and vacuum-dried overnight at 80 °C.

Characterization: FTIR spectrum was measured with Bruker ALPHA II equipped with Platinum ATR module (diamond crystal). Raman spectra were measured using Thermo Scientific DXRxi Raman Imaging microscope with 532 nm laser. The laser intensity was set to 1 mW.

Electrochemistry: Working electrodes were prepared by mixing **NiTTO** with Super P and poly(vinylidene difluoride) (PVdF) with a mass ratio of 5:4:1 in N-methylpyrrolidone (~250 mg NiTTO per 1 mL of the solvent). The resulting slurry was deposited onto Al foil by tape-casting, dried at 70 °C, vacuum-dried for 4 h at 100 °C, calendered at room temperature, and vacuum-dried again for 4 h 100 °C. The electrode composite areal loading was 2.2 mg cm^{-2}. CR2032-type coin cells were assembled in an argon-filled glovebox (O_2 <1 ppm, H_2O <0.1 ppm). Metallic potassium was used as an anode, 1.5M KPF_6 solution in dry 1,2-dimethoxyethane was used as an electrolyte (80 μL per cell), glass fiber filters were used as separators. Galvanostatic cycling was performed in the potential range of 1.3-3.6 V vs. K^+/K. Specific capacities and current densities were calculated per active material mass unit.

Operando Raman measurements: The working electrode was prepared the same way as for the other electrochemical studies, except for the mass ratio of **NiTTO**:carbon:PVdF, which was 8:1:1 for the Raman experiments. The electrode size was 1 mm x 10 mm. An electrochemical cell with an optically transparent glass window (ECC-Opto-Std, EL-CELL) was assembled in two-electrode configuration. Metallic potassium was used as the anode, 1.5M KPF_6 solution in dry 1,2-dimethoxyethane was used as the electrolyte, glass fiber was used for the separators. The cell was tested in cyclic voltammetry mode with a scan rate of 0.047 mV s^{-1} in the potential range of 1.3-3.6 V vs. K^+/K. The spectra were measured using Thermo Scientific DXRxi Raman Imaging microscope with 532 nm laser (1 mW power). Background signal from fluorescence was then subtracted with OriginPro 2019.

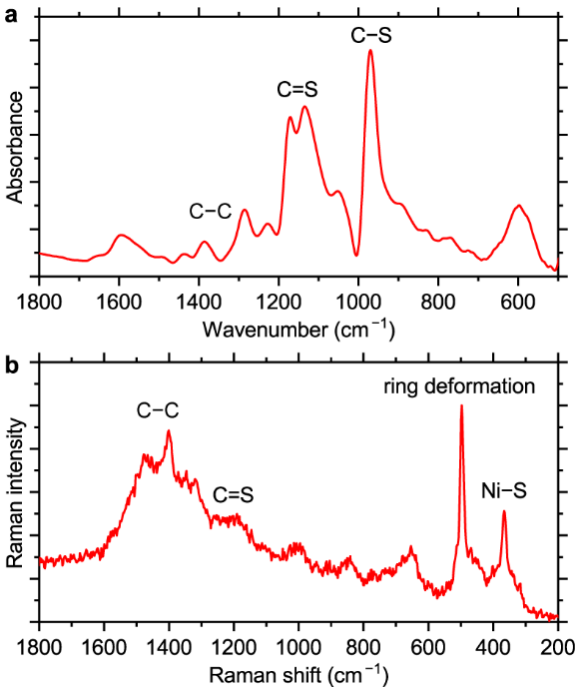

Figure S1. FTIR (a) and Raman (b) spectra of **NiTTO**.

Figure S2. Image of a separator of a **NiTTO**-based cell after cycling.

References

1 H. Poleschner, W. John, F. Hoppe, E. Fanghänel and S. Roth, *J. Prakt. Chem.*, 1983, **325**, 957-975.

2 G. Steimecke, H.-J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1979, **7**, 49-55.