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Nickel tetrathiooxalate as a cathode material for potassium batteries

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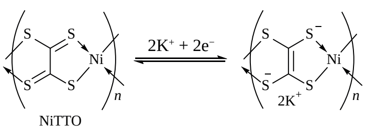
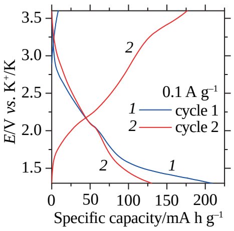
We report a nickel tetrathiooxalate (NiTTO) coordination polymer as a cathode material for potassium batteries. In a potential range of 1.3–3.6 V *vs.* K^+/K, the specific capacity of the material is 209 mA h g^{-1} at a current density of 0.1 A g^{-1}, which roughly corresponds to the two-electron reduction of polymer repeating units. The charge–discharge mechanisms of NiTTO in potassium cells were examined using *operando* Raman spectroscopy.





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Potassium-ion batteries have attracted attention as alternatives to widely used lithium-ion batteries.[1–5] In contrast to lithium, potassium is an abundant element, and it has a low reduction potential, which increases the battery voltage and energy density.[6,7] Additionally, K^+ ions have faster diffusion rates in battery electrolytes than those of Li^+ or Na^+ ions; this is useful for developing energy storage devices with high charge–discharge rates.[8,9] Lower reduction potential of potassium and faster diffusion of K^+ ions in the electrolytes make K-ion batteries advantageous over Na-based batteries, another promising alternative to Li-ion batteries,[10] although sodium leads to higher specific capacities.

However, K-ion battery cathode materials with high-rate capabilities are still underrepresented in the literature. Coordination polymers with π–d conjugation[11,12] are among the most promising fast-charging battery materials. These compounds have good conductivity (>1 S cm^{-1}),[11] which enables high charge transfer rates and allows one to reduce the amount of electrochemically inactive conductive fillers[13] and increase the overall battery capacity. These polymers are promising for energy storage devices.[13–22] However, none of them have been tested as cathode materials for potassium-based batteries. Here, we report nickel tetrathiooxalate (NiTTO), an electronically conductive coordination polymer,[23,24] as a cathode material for potassium batteries.

NiTTO was synthesized according to a published procedure[25] from 1,3,4,6-tetrathiapentalene-2,5-dione and nickel chloride. NiTTO is insoluble in water and organic solvents (ethanol, acetone, and dimethoxyethane). The FTIR and Raman spectra of the material were consistent with the literature data (Figure S1). The signals at 1300–1600 cm^{-1}, which had high intensity in Raman spectra and low intensity in FTIR spectra, corresponded to carbon–carbon bond vibrations;[18,26] the signals at 1100–1200 cm^{-1} corresponded to C=S bonds,[18,27] and a peak at 970 cm^{-1} in the FTIR spectrum was due to C–S bond vibrations.[18] Intense bands in the Raman spectrum at ~500 and ~370 cm^{-1} corresponded to the deformational vibrations of rings and Ni–S stretching vibrations, respectively.[27,28]

The electrochemical properties of NiTTO in potassium half-cells were studied in a potential range of 1.3–3.6 V *vs.* K^+/K. At a current density of 0.1 A g^{-1}, the charge and discharge capacities at the first cycle were 8 and 209 mA h g^{-1}, respectively [Figure 1(*a*)]. A low initial charge capacity indicates that the *n*-doping level of the material was negligible; that is, the ethenetetrathiolate

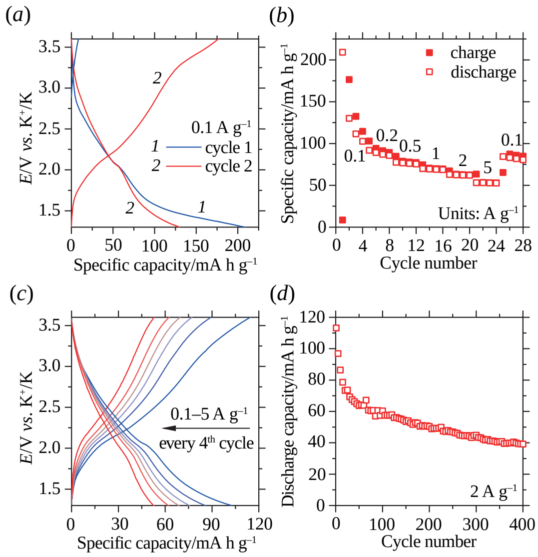

Figure 1 Electrochemical properties of NiTTO in potassium cells: (*a*) charge–discharge curves for the first two cycles at 0.1 A g^{-1}; (*b*) dependences of charge and discharge capacities on the cycle number for a varying current density; (*c*) charge–discharge curves for different current densities; and (*d*) cycling stability at 2 A g^{-1}.

moieties ($C_2S_4^{4-}$) were almost completely oxidized to tetrathiooxalates ($C_2S_4^{2-}$).[23]

The initial discharge capacity roughly corresponds to the theoretical capacity for two-electron reduction of NiTTO repeating units. The charge capacity at the second cycle was 176 mA h g^{-1}. After four charge–discharge cycles, the capacity became relatively stable at ~90–100 mA h g^{-1}. The main reason for the capacity decay was the dissolution of NiTTO reduction products, which was indicated by the intense coloring of separators after cycling (Figure S2).

Note that the capacity did not decrease with the current density. Even at 5 A g^{-1} (charging in < 40 s), the capacity reached 53 mA h g^{-1}, which was 63% of the capacity observed at 0.1 A g^{-1} for the subsequent cycle [Figure 1(*b*),(*c*)]. At the same time, the initial capacity at 2 A g^{-1} was 113 mA h g^{-1} [Figure 1(*d*)]. Since NiTTO has high electron conductivity, the material is expected to retain high-rate capabilities even with low carbon amounts in the electrodes.

To investigate the charge–discharge mechanisms of NiTTO in potassium cells, we used *operando* Raman spectroscopy. In the charged state, the Raman spectra corresponded to the initial NiTTO material [Figure 2(*a*)]. During the potassiation, the C=S band intensity at 1100–1200 cm^{-1} decreased. The Ni–S stretching vibration frequency decreased from 369 to 355 cm^{-1}. Additionally, a peak at 485 cm^{-1}, which corresponds to ring deformational vibrations, disappeared, and another peak appeared simultaneously at 452 cm^{-1}. These changes in the Raman spectra were reversible. Based on the Raman spectroscopic and electrochemical data, we concluded that the two-electron reduction of tetrathiooxalate moieties to ethenetetrathiolate units occurred during discharge [Figure 2(*b*)]. A similar mechanism was observed previously in sodium-based cells.[18]

To summarize, the nickel tetrathiooxalate complex was studied as a cathode material for potassium batteries, and its charge–discharge mechanisms were investigated using *operando* Raman spectroscopy. NiTTO can become a promising cathode material for fast-charging batteries if the dissolution of its reduction products is suppressed, for example, by tuning the electrolyte composition.

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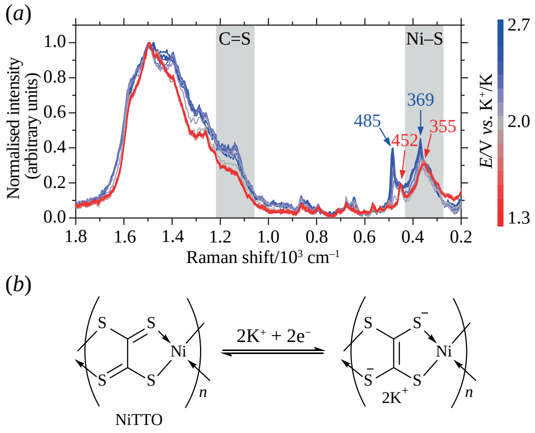

Figure 2 (*a*) *Operando* Raman spectra of NiTTO at different potentials and (*b*) charge–discharge mechanism proposed for NiTTO.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.024.

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