Electrochemical Performance of Layered FeSe for Sodium Ion Batteries Using Ether-Based Solvents

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We have evaluated layered FeSe as the anode in sodium ion batteries using an ether-based electrolyte. The maximum first irreversible capacity and efficiency are 294 mAh g⁻¹ and 87.2%, respectively. From XRD analysis, intercalation of Na ions between the selenide double layers of the layered FeSe occurred in the early stages of the first charging, which was followed by the formation of an amorphous Na-Se structure. Nevertheless, FeSe demonstrated good cycle performance and rate capability, with a discharge capacity retention ratio of 90% after 100 cycles and 75% at a current rate of 1.0 A g⁻¹ (~3C). Overall, the results presented herein suggest that FeSe has potential to function as the anode in sodium ion batteries.

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Experimental

Synthesis of FeSe.—FeSe powder was synthesized as follows. Powders of Fe and Se were mixed stoichiometrically and pressed into pellets. The pellets were sealed in an evacuated quartz tube, heated at 1027 °C for 30 h, then cooled down to 400 °C and annealed for 50 h, before finally being quenched in water. The resultant pellets were pulverized into powders. Note that the obtained FeSe sample included a small amount of Fe₃Se₄.

Electrode preparation.—The FeSe powder as the active material, carbon powder as the conductive additive, and polymeric acid at a solid weight content ratio of 80:10:10 were mixed in 1-methyl-2-pyrrolidione to form a slurry. The slurry was coated onto Cu foil (15 μm) and evaporated at 120 °C for 5 min. The electrode was then rolled into discs with a typical diameter of 10 mm. The cyclodehydration to form the polyimide was performed by heating at 350 °C for 30 min in a vacuum. The active material weight in the electrode ranged from 1.0 mg to 1.2 mg.

CR2032 cell preparation.—A CR2032 coin-type cell was assembled in an Ar-filled glove box. Na metal was used as the counter electrode. A trilayer separator (Celgard 2320, Celgard Corp.) and glass fiber filter (GB-100R, Advantech) were used as the separator, which were placed on the sides of the FeSe electrode and Na metal, respectively. For the liquid electrolyte, 1 M NaPF₆ was dissolved in diethylene glycol dimethyl ethyl (G2) (Kanto Chem.).

Electrochemical evaluation.—Cyclic voltammetry (CV) was performed at a scan rate of 0.1 mV s⁻¹. The lower cutoff voltages (LCVs) were 0.5, 1.0, and 1.3 V vs. Na/Na⁺. The upper cutoff voltage was 2.0 V. First and second charge–discharge at a current rate of 0.2 A g⁻¹ with various cutoff voltages were investigated during initial charge–discharge, and the cycle performance was evaluated after the initial charge–discharge. After 50 cycle tests were conducted at a current rate of 0.2 A g⁻¹, 10 cycles at current rates of 0.2, 0.5, 1.0, 2.0, and 4.0 A g⁻¹ were evaluated, giving rise to a total of 100 cycles. All electrochemical evaluations were performed at a range from 23–26 °C.

Analysis.—The FeSe crystal structure was characterized by X-ray diffraction using Cu Kα radiation (Ultima, Rigaku). Because the sintered samples were unstable in air, they were covered with a Kapton film to avoid exposure to air during the measurements. The microstructure was observed using field emission scanning electron microscopy (FE-SEM, Hitachi S-4300E). AC impedance analysis was performed using a Solartron 1260A frequency response analyzer in the frequency range.
range from 100000 to 0.05 Hz with an AC signal amplitude of 30 mV in the open circuit state. ZView from Scribner Associates Inc. was used as the AC impedance analysis program.

Results and Discussion

FeSe electrode characterization.—As seen in Fig. 1a, the XRD pattern of the FeSe electrode indicates that FeSe has a high degree of c-axis preferred orientation. Additionally, the 001, 002, and 101 reflections are observed. As shown in the corresponding SEM image (Fig. 1b), the synthesized powders have a broad particle size, ranging from several tens of microns to sub-micron.

Cyclic voltammograms of FeSe using G2 solvent with various LCVs.—Fig. 2 shows the first CVs of the FeSe electrodes. While reduction (charge) peaks were observed at 1.30, 1.15, and 0.68 V, oxidation (discharge) peaks were observed at 1.28, 1.55, and 1.65 V. From the correlation between the increase in the current peak and the cutoff potential, the reduction peaks at 1.30, 1.15, and 0.68 V appear to correspond to the oxidation peaks at 1.55, 1.65, and 1.28 V, respectively. Several small oxidation current peaks from 1.8 V to 2.5 V were observed, corresponding to the reduction at 1.28 V. The potentials at the current peak differ largely for reduction and oxidation, suggesting that their corresponding electrochemical reactions differ.

First charge–discharge curves and structural changes of FeSe using G2 solvent with various LCVs.—Fig. 3a shows the first charge–discharge curves with various LCVs at a current rate of 50 mA g$^{-1}$. For LCVs of 0.5, 1.0, and 1.3 V, the charge capacities are 337, 165, and 35 mAh g$^{-1}$, and their efficiencies are 87.2, 76.9, and 62.5%, respectively. The observed reversible capacity of FeSe (294 mAh g$^{-1}$) was smaller than its theoretical value (388 mAh g$^{-1}$) calculated from Equation 1. We attribute this difference to the LCV and current rate not being completely optimized.

\[
2\text{Na}^+ + \text{FeSe} \rightleftharpoons \text{Na}_2\text{Se} + \text{Fe} \tag{1}
\]

Figs. 3b and 3c show the XRD patterns of the charge and discharge states (indicated with black allows), respectively. At a charge...
state of 0.5 V vs. Na/Na$^+$, only an amorphous FeSe structure was observed. By comparison, only an intercalated structure was observed at a charge state of 1.0 V. A sharp reflection is shown at \( \theta = 12.85 \) degree, which is composed of the (002) reflection of Na$_x$FeSe indexed on the ThCr$_2$Si$_2$ structure with lattice parameters \( c = 13.81 \) Å.\textsuperscript{28} Pristine and intercalated structures of FeSe were observed at a charge state of 1.3 V, demonstrating that phase separation between the intercalated and pristine states occurred during charging. Although we did not confirm the co-intercalation of sodium ions with the ether-based solvent, co-intercalation may occur in charging states earlier than that at 1.3 V. In the 1.5 V discharge state, a pristine structure was observed only in the electrode after charging at 1.3 V. Further, the Fe$_7$Se$_8$ impurity phase persisted. The electrodes after charging at 1.0 and 0.5 V showed an amorphous structure at discharge state. These results indicate that the intercalated structure of FeSe at the charge state changes to an amorphous structure during discharge.

**Cycle and rate performances of FeSe electrodes.**—Figs. 4a and 4b show the cycle performance and rate performance of FeSe electrodes. The cell with a LCV of 0.5 V showed superior cycle performance to that with a LCV of 1.3 V after 100 cycles. For instance, the discharge capacities (retention ratios) of the cells with LCVs of 0.5 and 1.3 V were 267 (90%) and 35 mAh g$^{-1}$ (62%), respectively. Clearly, deeper LCVs are unable to accelerate degradation of the cycle performance in FeSe, though higher cutoff voltages may significantly influence cycle performance. Fig. 4c shows the impedance spectra in the discharge state after the 10th and 100th cycles. Semicircles are observed in all of the AC impedance spectra, and their sizes before and after 100 cycles are almost identical. Therefore, these electrolytes only showed slight decomposition during the cycle tests. The XRD patterns of the FeSe electrode at discharge state after 100 cycle tests are shown in Fig. 4d. As indicated, only an amorphous FeSe structure is present. Although pristine phase was observed in the cell at a LCV of 1.3 V after the first charge–discharge, the pristine phase was not observed in the electrode after 100 cycle tests, indicating that the layered FeSe structure changed to an amorphous structure during cycles.

**Discussion.**—The layered FeSe structure changed to an amorphous structure during charge–discharge as shown schematically in Fig. 5. Ultimately, only an amorphous structure was observed regardless of the LCV following the cycle tests. However, good cycle performance was observed for the cell using FeSe as the anode for the sodium ion battery. We attribute the improved cycle performance to relatively small volume changes of the amorphous structure during charge–discharge. In particular, in the case of LCV = 0.5 V better cycle performance was obtained. We consider that the keeping a voltage lower in the first charging is important to induce homogeneous electrochemical reaction in the FeSe electrode during the cycling test. Almost particles were of the amorphous phase in LCV = 0.5 V, which would prevent the desorption of particle from the electrode because of little local distortion, and as a result, better cycle performance was obtained.

Good cycle performance of FeSe was observed in the presence of an ether-based solvent, which is highly stable in the reduction state. As shown in Fig. 6, FeSe using a carbonate solvent did not exhibit good cycle performance.

**Conclusions**

We have demonstrated that FeSe functions as an effective anode for Na-ion batteries in the presence of an ether-based solvent. However, confirmation of the co-intercalation of Na ions and this solvent was not established. The structure of FeSe became amorphous in the first discharge. The discharge capacity retention ratio after 100 cycles and rate capability were 90% and 75% (1 A g$^{-1}$/0.2 A g$^{-1}$), respectively.
Overall, FeSe is found to be a promising anode material for sodium ion batteries.

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Figure 5. Schematic representation of structural changes in FeSe during charge–discharge.

Figure 6. Cycle performance of FeSe using various solvents at the current rates of 0.2 A g\(^{-1}\). Black plots and blue plots are using EC/DEC solvent and G2 solvent, respectively.