Electrochemical property of low crystalline VS_4 electrode material prepared by mechanical milling

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Elemental sulfur is one of the attractive positive electrode materials because of its high theoretical capacity (1672 $mAh \cdot g^{-1}$). However, there are the several severe problems such as the dissolution of lithium polysulfide (Li_2S_n, n>2) into the organic electrolytes and low electronic and ionic conductivity of S, which cause the low cycle life and energy efficiency. To resolve these problems, we propose utilizing the transition-metal sulfides as a positive electrode material of the Li-S batteries.[1-3] Among several candidates, VS_4 is promising because of its high theoretical capacity (1197 $mAh \cdot g^{-1}$). In the present work, the analysis of discharge/charge mechanism using X-ray absorption and total scattering measurements suggested the formation of a low crystalline phase similar to VS_4 at first cycle and discharge/charge reactions would proceed reversibly from second cycle.[4] For further improvement of electrochemical performance, the synthesis of VS_4 with similar local structure as VS_4 after structural change at the initial discharge and charge would be an effective way.

In this work, we employed mechanical milling process at room temperature to prepare low crystalline VS_4 and evaluated its electrochemical property. Crystalline VS_4 prepared with heat treatment at 400˚C under vacuum sealing in a glass tube was used as the starting material. In powder XRD patterns of VS_4 prepared with mechanical milling, the clear diffractions from the crystalline VS_4 decreased and broadened, indicating that crystallinity of VS_4 lowered with mechanical milling. The electrochemical property of the VS_4 positive electrode materials was evaluated with carbonate-based electrolyte and Li metal anode at 1/20 C in the voltage range of 1.0 – 3.0 V. VS_4 positive electrode materials showed high discharge capacity of ca 950 $mAh \cdot g^{-1}$. The voltage plateau in first discharge of the low crystalline VS_4 rose to 2.0 V, while that of the crystalline VS_4 showed 1.9 V. Furthermore, charge capacity and columbic efficiency at first cycle increased by ca 100 $mAh \cdot g^{-1}$ and ca 10% respectively in the low crystalline VS_4.

The details of the mechanism for improvement of electrochemical performance is currently investigated. We believe lowered crystallinity improves the electrochemical performance and is a key to design polysulfide electrode materials with high energy density.

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References

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