Elemental sulfur is one of the attractive positive electrode materials because of its high theoretical capacity (1672 mAh·g⁻¹). However, there are several severe problems such as the dissolution of lithium polysulfide (Li₂Sₙ, 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. Among several candidates, VS₄ is promising because of its high theoretical capacity (1197 mAh·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 VS₄ at first cycle and discharge/charge reactions would proceed reversibly from second cycle. For further improvement of electrochemical performance, the synthesis of VS₄ with similar local structure as VS₄ 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 VS₄ and evaluated its electrochemical property. Crystalline VS₄ 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 VS₄ prepared with mechanical milling, the clear diffractions from the crystalline VS₄ decreased and broadened, indicating that crystallinity of VS₄ lowered with mechanical milling. The electrochemical property of the VS₄ positive electrode materials was evaluated with carbon-based electrolyte and Li metal anode at 1/20 C in the voltage range of 1.0 – 3.0 V. VS₄ positive electrode materials showed high discharge capacity of ca 950 mAh·g⁻¹. The voltage plateau in first discharge of the low crystalline VS₄ rose to 2.0 V, while that of the crystalline VS₄ showed 1.9 V. Furthermore, charge capacity and columbic efficiency at first cycle increased by ca 100 mAh·g⁻¹ and ca 10% respectively in the low crystalline VS₄.

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