Operando Raman and Impedance Spectroscopy Investigation of Magnesium-Sulfur Batteries

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Due to their high theoretical specific capacity, potentially low costs, and intrinsic safety, magnesium/sulfur (Mg/S) batteries are one of the most promising next generation battery systems. However, the reaction mechanism in these batteries has so far been hardly explored. Here, we show a room-temperature Mg/S battery with a highly sulfur loaded cathode (~3 mg cm\textsuperscript{-2}), using a nitrogen doped graphene-multiwall carbon nanotube carbon host matrix and Mg\textsubscript{2}B(hfip)\textsubscript{4} as electrolyte. \textit{Operando} Raman spectroscopy is employed to investigate the formation of polysulfide species at the cathode of Mg/S cells during the charge/discharge and density functional theoretical (DFT) calculations are used to correlate the Raman modes with a series of polysulfide species (S\textsubscript{x}\textsuperscript{n-}, x=1-8). The \textit{operando} Raman measurements show the chemical transformation from elemental sulfur (S\textsubscript{8}) via long and short chain polysulfides to magnesium sulfide upon discharge and conversion back to elemental sulfur during charging. Furthermore, the spectral measurements indicate the formation of a nanocrystalline cubic sphalerite magnesium sulfide phase at the end of discharge. The self-discharge study of Mg/S cells using operando Raman spectroscopy and operando impedance spectroscopy shows the reduction of S\textsubscript{8} to higher order polysulfides under open circuit potential (OCV), leading to an increase of the cell resistance. The present report also investigates the evolution of cathode, anode, and total cell impedances during different states of charge/discharge (SOC) and formation of the passivation layer at the Mg anode side.

Keywords: magnesium/sulfur battery, nitrogen doped carbon, \textit{operando} Raman spectroscopy, density functional theoretical calculations, impedance spectroscopy, X-ray photoelectron spectroscopy

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