

Enhanced Energy Density and Redox Kinetics in Aqueous Polysulfides beyond the Solubility Limit

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The low cost, high solubility, and high volumetric capacity of aqueous polysulfide electrodes are attractive for battery applications. Our group developed a redox flow battery system using an air (oxygen) cathode and an aqueous polysulfide anode, aiming at low-cost, large-scale grid storage.^[1] Techno-economic modeling showed that for ultralow-cost active materials such as sulfur, the auxiliary components including tank and supporting electrolyte cost more than the active materials themselves. Therefore, increasing the volumetric capacity reduces the auxiliary component content, and further reduces the energy cost. Here, we demonstrate two paths to this goal. One is the cycling of concentrated aqueous polysulfides beyond the solubility limit of the shortest chain polysulfide (i.e. Na₂S₂). This is shown to enhance the reversible volumetric capacity up to 10M total sulfur concentration. However, the formation of insulating precipitates on the planar current collector increases the ohmic resistance and slows mass transport of active species.

Our second approach adds a percolating nanoscale conductive network to the reversible precipitating electrode. Carbon nanoparticles are suspended in the aqueous polysulfide electrolytes to form conductive networks that provide electronic contact throughout the electrode. Such an “infinite current collector” strategy was demonstrated by our group in other electrochemical applications including lithium-ion^[2] and lithium-sulfur batteries.^[3] We first systematically study the effect of carbon content using galvanostatic cycling experiments. Then, galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) were used to gain insight into transport kinetics at different stages of precipitation of the sodium polysulfide, Na₂S_x. GITT analysis reveals that as precipitation occurs, the internal resistance (summation of bulk resistance and charge transfer resistance) decreases, but active species diffusion also slows. EIS analysis indicates that the benefit of the decreasing charge transfer resistance exceeds that of an increasing bulk resistance during the precipitation process; surprisingly, internal resistance drops as precipitation occurs. The decreased charge transfer resistance is attributed to the precipitated solid sodium polysulfide acting as an electrocatalyst for polysulfide redox. In summary, we demonstrate a highly reversible precipitating aqueous polysulfide electrode with enhanced rate capability by utilizing conductive nanoparticle suspension.

References:

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[3] F. Y. Fan, W. H. Woodford et al., *Nano Lett.* 14 (2014) 2210-2218.