

Understanding the Role of Solvent and Added Water on the Effectiveness of Lithium Iodide as a Redox Mediator in Lithium Oxygen Batteries

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Non-aqueous lithium oxygen batteries have been the subject of intense research interest over the past decade or two, owing to their very high theoretical gravimetric energy density; potentially up to three times that of state-of-the-art lithium ion batteries¹. Despite this widespread effort, lithium oxygen batteries still suffer from a number of significant issues, including high overpotential on charge and poor cycle life¹. Part of this poor charging performance can be attributed to the insulating nature of the lithium peroxide formed on discharge, which makes direct electrochemical oxidation challenging. While a number of previous approaches have focused on conventional surface based catalysis², this approach can be ineffective as only a limited amount of the lithium peroxide is in contact with the electrode surface and it can become electrically isolated from the electrode during charge, or even form during discharge without electrical contact with the electrode surface³. In response to these short-comings of solid-state catalysts, there has been considerable interest in soluble redox mediators as a means of improving the charging process^{2,4,5}.

Lithium iodide, in particular, has shown very promising performance as a soluble redox mediator for lithium oxygen batteries^{4,5}. Despite this promise, there has been serious ambiguities in literature relating to the influence of lithium iodide on both the discharge and charge processes. In a recent work, we have helped explain how lithium iodide influences the product formed during discharge; shifting from Li₂O₂, to LiOH, to LiOH-H₂O and LiOOH-H₂O depending on the amount and chemical environment of water present in the electrolyte². In this work, we provided a detailed framework for understanding how these various discharge products can be oxidized during charge based on solvent properties as well as the amount of water present in the electrolyte. The importance of differing interactions between iodide, triiodide and iodine with glyme-based electrolytes and added water is discussed and a number of important behavior transitions at differing water concentrations are uncovered.

References:

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