Investigating the Dehydration Mechanism of Disodium Hydrogen Phosphate Dodecahydrate for Thermal Management in Lithium-Ion Batteries

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Thermal management strategies are becoming increasingly important with the rise in the use of lithium-ion batteries (LIB), as these batteries often require cooling and are at risk of thermal runaway and fires. [1,2] One proposed method to cool LIBs and prevent thermal runaway, is in the application of phase-change materials (PCMs) and thermochemical materials (TCMs) to act as a heat buffer as part of a battery thermal management system. [1, 3] Salt hydrates are possible candidate PCM and TCM materials and are particularly attractive as they are non-flammable and environmentally benign. [2] Disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4.12H_2O$) is one such material that has potential for use in this application. This material can act as both a PCM, undergoing a solid to liquid phase change, with a melting point of 35 °C, which can maintain the battery safe working temperature and as a TCM, through an endothermic stepwise dehydration which could prevent thermal runaway. [4, 5] Understanding the dehydration mechanism is vital for the implementation of salt hydrates as thermal protection materials, investigating how the environment affects the dehydration temperature and hydration state. The dehydration mechanism has primarily been studied using thermogravimetric analysis (TGA) and thermo-Raman spectroscopy. There are conflicting views in the literature, with different proposed dehydration pathways, transitioning through different hydration states. [5, 6] Further complicating the dehydration mechanism, $Na_2HPO_4.12H_2O$ rapidly dehydrates at ambient conditions, which makes studying structural changes very challenging. [4]

This work explores the dehydration mechanism of $Na_2HPO_4.12H_2O$, through combined *in-situ* x-ray powder diffraction – differential scanning calorimetry (XRPD-DSC) studies alongside TGA-DSC. DSC-XRPD enables studying the dehydration *in-situ* by collecting simultaneous XRPD with increasing temperature, whilst monitoring the thermal behaviour. We have further monitored the behaviour of this materials under different conditions of humidity and temperature using XRPD-DSC.

These measurements allow the crystal structural changes to be monitored as a function of temperature and humidity to identify the different hydration states that form and therefore define the dehydration mechanism more clearly than the published TGA and Raman studies. These results allow the relative stability and dehydration pathways of $Na_2HPO_4.12H_2O$ and its other hydrates to be determined in application environments, which is invaluable for the optimisation and implementation of $Na_2HPO_4.12H_2O$ as a TCM in thermal-protection applications.

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