ABSTRACT

Lithium-ion batteries (LIBs) are currently a mainstay of electrochemical energy storage systems due to their high energy density, cycle lifetimes, and portability, seeing widespread use across applications such as consumer electronics, renewable energy storage, and electric vehicles. However, the scarcity and uneven geographical distribution of lithium and other raw materials required for LIBs in the Earth's crust raises questions about its long-term sustainability, both from a resource management and economic perspective. The safety of LIBs is also an area of paramount importance, as once thermal runaway is initiated there is currently limited recourse to prevent catastrophic cell failure, which can be disastrous for such a widely utilized technology. Therefore, alternatives to lithium as charge-carrying ions for batteries are under active research investigation, and the limited lithium resources that are readily available must be used judiciously.

Potassium-ion batteries (KIBs) are a promising alternative to LIBs as potassium itself is over one thousand times more abundant in the Earth's crust than lithium, in addition to the potential elimination of other problematic metals commonly used in LIBs such as cobalt. However, the electrochemical performance of KIBs significantly lags behind LIBs, especially on the fronts of energy density and cycling stability. Many of these issues can be traced to the larger ionic radius of potassium ions compared to lithium ions (1.38 Å vs. 0.76 Å), which begets an increased volumetric expansion of KIB electrodes over cycling and subsequent mechanical stresses that reduce the overall cycling stability. Strategies to mitigate these effects can be employed on the design of both the electrodes and the electrolyte to help KIBs achieve satisfactory performance targets.

On the electrolyte side, the cyclic ethers tetrahydropyran (THP) and tetrahydrofuran (THF) are investigated as electrolyte solvents for their weakly solvating properties compared to standard KIB electrolytes. The weakly solvating nature of THP and THF are conducive towards creating an anion-dominated solvation environment around K^+ in the bulk electrolyte, which leads to the formation of more robust passivation layers on the Prussian blue analogue (PBA) cathode surface and K metal anode surface. This translates to an observed increase in capacity retention and Coulombic efficiency in the cycling of K metal||PBA cells, and the choice of THP or THF as the electrolyte solvent can be made to accommodate cathodes of various operating voltage windows.

On the electrode side, the synthesis of PBA cathodes was investigated to explore methodologies by which the resulting PBAs could have their electrochemical properties tuned. Three different naturally occurring potash materials were incorporated into the aqueous co-precipitation synthesis of PBAs, including two different purity grades of KCl and langbeinite, a commonly used fertilizer. When the high purity KCl was used in the PBA synthesis the observed specific capacity was increased, and when langbeinite was used the capacity retention and rate capability were improved as compared to the non-modified PBA cathodes.

Lastly, the safety characteristics of a novel niobium tungsten oxide (NbWO) anode and cyclopentyl methyl ether (CPME)-based electrolyte for LIBs were studied. NbWO and CPME have been used in combination to enable impressive fast-charging and low temperature performance, and their safety was benchmarked next to the standard graphite anode and carbonate-based commercial electrolyte used for LIBs. The volatility of CPME contributed to a higher measured exothermic heat release under thermal stress compared to the commercial electrolyte, though the cycled NbWO anodes generated much less exothermic heat than the graphite anodes due to the lack of a thermally unstable solid-electrolyte interphase (SEI) layer. Taken together, the new NbWO/CPME electrolyte LIB system outperformed the standard graphite/commercial electrolyte LIB from a heat generation perspective, demonstrating its potential efficacy as an LIB tailored towards specific applications for which exceptional fast-charging and low temperature performance are required.