## Ether Electrolytes Enable Ultrastable and Energy-Efficient High-Voltage Sodium Metal Batteries

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Ether electrolytes have been demonstrated to be well compatible with sodium metal electrodes. However, stable cycling of sodium positive electrodes in ethers is largely limited to those with low working potentials (<3.5 V vs Na<sup>+</sup>/Na), but rarely achieved for higher potential positive electrodes. Here, we demonstrate that the use of an 1 M NaPF<sub>6</sub>-diglyme solution enables the very stable cycling of the high-potential Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> material, displaying an average working potential around 3.95 V vs Na<sup>+</sup>/Na. The above-mentioned positive electrode material shows an unprecedented high capacity retention (96.2% at 64 mA g<sup>-1</sup>, i.e., 0.5 C, after 300 cycles) and an outstanding rate capability (120.2 mAh g<sup>-1</sup>, 111.6 mAh g<sup>-1</sup>, and 85.3 mAh g<sup>-1</sup> at 1280 mA g<sup>-1</sup> (10 C), 2560 mA g<sup>-1</sup> (20 C) and 6400 mA g<sup>-1</sup> (50 C), respectively), resulting from the effective polymer-inorganic interphase formed at Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> surface. Moreover, sodium metal batteries (SMBs) employing Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> positive electrodes exhibit extremely low heat generation due to the significantly alleviated cell polarization in this ether electrolyte, which is extremely appealing for safe and efficient energy storage.

Submitted: 30.09.2020

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