Abstract

Today, Li-ion batteries are the ultimate rechargeable energy storage systems; however, after decades of improvements, the technology might reach its energy-density limits. Ca batteries represent a promising electrochemical systems alternative to Li-ion one. The abundance of Ca, its low redox potential, only slightly higher than that of Li and high volumetric capacity make Ca metal batteries an attractive energy storage for the future. However, the development of Ca batteries is hindered due to the lack of efficient electrolytes able to reversibly strip/deposit calcium at room temperature and with high electrochemical window stability. The objective of this project is to develop and test both new electrolytes and new electrode materials for room temperature batteries by transferring the experience from the Mg systems. Herein, we synthesised at room temperature high purity fluorinated alkoxyborate salt $Ca[B(hfip)_4]_2\times 4DME$ and use it in calcium electrolyte. Reversible Ca plating/stripping at room temperature and a wide electrochemical stability up to 4 V vs. Ca/Ca^{2+} were evidenced. Further, we demonstrated that anthraquinone-based polymer could be used as cathode material to develop high energy density Ca-organic batteries. Electrochemical mechanism investigation confirms the reversible reduction of the carbonyl bond of anthraquinone backbone and coordination with Ca^{2+} cations in the discharged state. Finally, we combined calcium anode and appropriate sulfur-based cathode to report a reversible electrochemical activity at room temperature of Ca/S battery proof-of-concept. This innovative system is characterized by a medium-term cycling stability with high specific capacity. Insights into the electrochemical mechanism governing the chemistry of the Ca/S system were obtained for the first time by combining XPS and XAS spectroscopy. The reversible electrochemical activity implies the formation of different types of soluble polysulfide species during both charge and discharge. These promising results open the way to the comprehension of emerging Ca/S systems.