Electrochemical energy storage beyond lithium is highly relevant for sustainable energy technology. New electrode concepts are needed for the intercalation of larger monovalent (Na\(^{+}\), K\(^{+}\)) or multivalent ions (Mg\(^{2+}\)). One example for a promising Na-ion battery is presented based on symmetrical NASICON-structured Na\(_2\)VTi(PO\(_4\))\(_3\) electrodes [1]. Operando synchrotron diffraction and absorption spectroscopy unravel the underlying sodium storage and charge compensation mechanisms. Model systems for multivalent-ion insertion are also hybrid batteries with two mobile metal ions in the electrolyte, where Mg is plated at the negative electrode, while Li- or Na-ions are inserted at the positive electrode [2, 3]. Recent results on the working mechanisms in such hybrid batteries are revealed by operando synchrotron diffraction and ex situ XPS. Appropriate material combinations for Mg-batteries with insertion-type positive electrodes and sufficiently high cell voltages are still lacking. For example, V\(_2\)O\(_5\) works only with unstable electrolytes in contact with Mg-metal and steel housing. The Mg-insertion mechanism was therefore investigated for a full cell with MgxMo6S\(_8\) as a suitable negative electrode [4].

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