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In-situ Transmission Electron Microscopy Study of Electrochemical Lithiation and Delithiation Cycling of RuO_2 Nanowires as Conversion Anodes

Yang Liu[2], Keith Gregorczyk[1], John Sullivan[3], and Gary W. Rubloff[1]

[1]Department of Materials Science & Engineering and The Institute for Systems Research, University of Maryland, College Park, MD 20742

[2]Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico, 87185

[3]Sandia National Laboratories, Livermore, California, 94551

Abstract: Ruthenium Dioxide (RuO_2) is a conversion type negative electrode with a number of attractive properties, such as low resistivity (~30 μΩ•cm) and high theoretical capacitance (1410 mAh/g). Therefore, RuO_2 is ideal for studying conversion type electrodes with applications in Li-ion batteries. The reaction mechanism, however, has only been investigated for large (micron) powders mixed with binders and carbon black, never in its pure form and never with in-situ transmission electron microscopy (TEM). Furthermore very little in-situ work has been done on conversion electrodes in general. In this work, electrochemical lithiation/delithiation cycling of single crystal RuO_2 nanowires was conducted inside a TEM. In the first lithiation cycle, a two-step phase transformation was observed: (1) Li intercalation into crystalline RuO_2 (Tetragonal, S.G.: $P4_2/mnm$) formed intermediate crystal phase Li_xRuO_2 (Orthorhombic, S.G.: Pnnm), where x is close to 1; (2) further lithiation converted the crystalline Li_xRuO_2 to nanocrystalline Ru embedded in Li_2O matrix. From the first delithiation process and the subsequent cycles, a reversible conversion reaction between Ru/Li_2O composite and amorphous RuO_2 took place. Part of the reaction was irreversible, a conclusion supported by the HRTEM and HAADF STEM images, showing that some Ru nanoparticles were embedded in the Li_2O after 3 lithiation/delithiation cycles. The nanowires became brittle and cracks were formed during cycling. These results provide a new understanding about the conversion reaction mechanisms in lithium ion batteries, and can be extended to other systems, such as RuO_2 grown or deposited with other systems (ALD, ECD, …), and other conversion type electrodes, such as Fe_2O_3, NiP, FeF_2, etc.

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