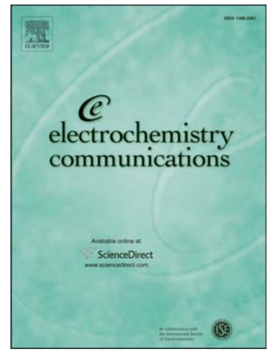
Accepted Manuscript



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PII: S1388-2481(16)30236-3
DOI: doi: 10.1016/j.elecom.2016.09.026
Reference: ELECOM 5796

To appear in: *Electrochemistry Communications*

Received date: 19 August 2016
Revised date: 29 September 2016
Accepted date: 29 September 2016

Tracking the structural evolution at atomic-scale in the spinel Mn_3O_4 induced by electrochemical cycling

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ABSTRACT

Mn_3O_4 is a possible candidate for use as an electrode material and has been found to undergo structural transformation during electrochemical cycling. Clarifying the transformation process is important in developing methods for improving electrochemical performance. Here, using scanning transmission electron microscopy (STEM) combined with the electron energy loss spectroscopy (EELS) technique in aberration-corrected TEM, we succeeded in tracking the structural evolution at an atomic-scale and identified the intermediate stage as rock-salt-structured MnO. A reasonable route was deduced via which the spinel Mn_3O_4 was transformed firstly into MnO and then into MnO_2.

Keywords: Mn_3O_4; electrochemical cycling; MnO; MnO_2; STEM-EELS

1. Introduction

Spinel transition metal oxides exhibit superior electrochemical performance characteristics in applications including energy conversion and storage systems, and for this reason are attracting considerable scientific attention [1,2]. Mn_3O_4 is a candidate electrode material for catalyzing the oxygen reduction reaction and electrochemical capacitance [3,4]. For many electrode materials in use, structural evolution usually occurs on the surface layer as electrochemical cycling takes place; this in turn has a strong influence on the resulting electrochemical properties [5-15], as demonstrated by changes in electrochemical performance. Clarifying the structural changes that occur in manganese oxides during cycling is therefore very important in improving their electrochemical performance. Previous studies have shown that Mn_3O_4 is converted into birnessite MnO_2 during voltammetric cycling in aqueous Na_2SO_4 electrolyte [16,17]. Although the final conversion product has been extensively studied by XRD, SEM and Raman scattering techniques, little attention has been given to the process by which this change occurs. Tracking the partially transformed state and capturing detailed structural and chemical information is key to identifying the intermediate products and further understanding the structural evolution of the spinel Mn_3O_4.

In the past few years, Fourier transform infrared spectroscopy (FTIR), synchrotron X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy have been used to identify structural changes involving chemical bonds or lattice structures [18-21]. However, these methods are not very suitable for studying changes in structure and chemistry that occur at an atomic scale. Aberration-corrected HAADF (high angle annular dark field) STEM with EELS atomic resolution, on the other hand, is ideally suited for investigating structural transformations at sub-angstrom levels, capturing real-time direct images [22] which make it possible to monitor any structural

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