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Intercalation of Mg-ions in layered V$_2$O$_5$ cathode materials for rechargeable Mg-ion batteries

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Introduction

The development of functioning rechargeable Mg-ion batteries is still in its early stage, and a coarse screening of suitable cathode materials is still on-going. Within the intercalation-type cathodes, layered crystalline materials are of high interest as they are known to perform well in Li-ion intercalation batteries and are also increasingly being explored for Na-ion batteries. Here, we present an investigation of the layered material orthorhombic V$_2$O$_5$ which is a classical candidate for an ion-intercalation material having a high theoretical capacity. We present discharge-curves for the insertion of magnesium, and investigate the degradation as a function of cycle number. Furthermore, in an attempt to separate degradation associated with the cathode and the anode, effects of exchanging anode and electrolyte were investigated. Hereby, up to 50% of the cathode capacity was regained on the subsequent discharge. This indicates that the degradation is highly associated with formation of ion-blocking layers on the anode.

V$_2$O$_5$ – a layered material

Orthorhombic V$_2$O$_5$ consists of sheets of interconnected VO$_5$-units (Figure 1). Cations can be inserted in-between the layers via the reduction of vanadium. Inserting one and two Mg-ions can be written as follows:

$$\begin{align*}
V(5+)_2O_5 + Mg & \rightarrow MgV(4+)_2O_5 \\
MgV(4+)_2O_5 + Mg & \rightarrow Mg_V(3+)_2O_5
\end{align*}$$

Discharge behavior

In order to test the discharge behavior of V$_2$O$_5$, we made a coating on thick Al-foil using a mixture of V$_2$O$_5$, carbon and PVDF-binder. A Mg-metal disc was used as the anode, and Mg(ClO$_4$)$_2$ as the electrolyte. The battery OCV was roughly 1.5V vs. Mg/Mg$^{2+}$ and the battery was discharged to OV at a rate of C/60. XRD was used on the coating before and after the discharge to measure the changes in crystal cell dimensions.

During discharge, the voltage decreases continuously (Figure 2). The capacity is 540 mAh/g, which corresponds to the intercalation of almost 1.9 Mg ions per V$_2$O$_5$ unit$^2$. This is a very high capacity, and a property which makes V$_2$O$_5$ an interesting candidate as a battery cathode material.

Before discharge, XRD reveals the material to be V$_2$O$_5$ as expected (Figure 3). After discharge, the crystal cell from V$_2$O$_5$ is still present, but some of the peaks are shifted due to the expansion of the cell. Planned in-situ synchrotron measurements are expected to shed light on the exact nature of the intercalation mechanism.

Anode exchange

To get an idea of how much of the degradation of the capacity seen in electrochemical cycling is from the cathode and how much is from the anode, we set up an experiment where we cycled a battery cell until the capacity was virtually zero (Figure 4). The cell was then opened and the Mg-disc anode was exchanged with a fresh one, and a few drops of fresh electrolyte was added. It is clearly seen that a substantial part of the capacity is recovered. This indicates that much of the degradation happens on the anode side, likely due to the formation of a solid electrolyte interphase$^1$.

Planned experiments

In-situ synchrotron X-ray diffraction measurements offer the possibility to correlate the features seen in the charge-discharge curves with changes in the crystal structure. Using this technique, we hope to gain further insight into the mechanism behind the intercalation of magnesium ions into the V$_2$O$_5$ structure.

References

$^1$M.M. Huie et al. / Coordination Chemistry Reviews 287 (2015) 540–559
$^2$http://www.chemtube3d.com/solidstate/SS-V2O5.htm

Multiprobe tool

Simultaneous structural and electrochemical information

- How does the structure charge during charge and discharge?
- What is the ion insertion and extraction mechanism?
- Is this the same during charge and discharge?