The Electrochemistry of Zinc Nitride: A New Reaction Mechanism for Li-Ion Negative Electrodes

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Conversion materials used in negative electrodes for secondary Li-ion batteries were first introduced by Fuji with tin-based amorphous composite oxides (1). They exhibit a large capacity of over 600mAh/g. They were found to react with Li in a two-step process (2) expressed as follow.

$$M_xO_y + 2y\ Li^+ + 2y\ e^- \rightarrow x\ M + y\ Li_2O \qquad [1]$$
$$M + z\ Li^+ + z\ e^- \rightarrow Li_zM \qquad [2]$$

The metal oxide is broken down into a metal M dispersed in a lithia matrix, Li_2O (Eq.1). The latter remains inert upon cycling while the reversible capacity is provided by the alloying and de-alloying reactions of M with lithium (Eq.2). However more recently, MO oxides, where M is a transition metal that does not alloy with lithium such as Co, Fe, Ni or Cu, were reported to react with lithium as expressed in Eq.1, but the reaction was found to be reversible (3). Upon oxidation, M reacts with Li_2O to re-form MO as expressed in Eq.3.

$$MO + 2\ Li^+ + 2\ e^- \leftrightarrows M + Li_2O \qquad [3]$$

Ternary lithium transition metal nitrides have also been reported as promising negative electrode materials. Two groups have been distinguished. The $Li_{2n-1}MN_n$ nitrides, such as Li_3FeN_2 (4) and Li_7MnN_4 (5), crystallize in structures derived from the cubic anti-fluorite, while the $Li_{3-x}M_xN$ nitrides (6-9), where M is a transition metal such as Co, Ni and Cu, are iso-structural to the hexagonal layered Li_3N. The transition metal substitutes for Li between the Li_2N layers. In these materials, Li ions must be removed in order to reversibly react with lithium. The best candidate exhibiting good cycling stability and large capacity consists in $Li_{2.6}Co_{0.4}N$ with 700mAh/g.

In this paper a transition metal nitride is reported, for the first time, to exhibit reversible conversion upon reaction with lithium. In-situ and ex-situ x-ray diffraction analyses were performed and enabled the identification of the reaction of zinc nitride, Zn_3N_2, as a conversion reaction leading to the generation of the LiZn alloy in a βLi_3N matrix, the high-pressure form of Li_3N (Eq.4).

$$1/3\ Zn_3N_2 + 3\ Li^+ + 3\ e^- \rightarrow Li\ Zn + 2/3\ \beta Li_3N \qquad [4]$$

Solid Li_3N had been thoroughly studied for its high ionic conductivity (10-12). As opposed to conventional conversion materials exhibiting an inert Li_2O matrix, βLi_3N transformed into LiZnN upon oxidation (Eq.5).

$$Li\ Zn + \beta Li_3N \leftrightarrows 3\ Li^+ + 3\ e^- + LiZnN \qquad [5]$$

As observed with the MO oxides showing the reversible reaction of Li_2O (Eq.3), this nitrogen conversion reaction (Eq.5) was found to be reversible and occurred in parallel with the de-alloying and re-alloying reaction of LiZn into metallic Zn (Fig.1). This nitrogen conversion reaction presented also the advantage of occurring at lower potential than conventional conversion reaction, which leads to an increase in the voltage output of the battery when cycling versus the same cathode material.

Zn_3N_2 exhibited gravimetric and volumetric capacities, 1325mAh/g and 8240mAh/cc, respectively, that exceed by far the ones obtained with graphite (372mAh/g and 840mAh/cc). However, poor cycling stability was observed. The failure mechanism of Zn_3N_2 was investigated using x-ray diffraction as a function of cycle number and electrochemical techniques. Based on this study, LiZnN was identified as a promising negative electrode material exhibiting little irreversible capacity in the first cycle. Other materials, which also act as reversible conversion nitrides, will be discussed.

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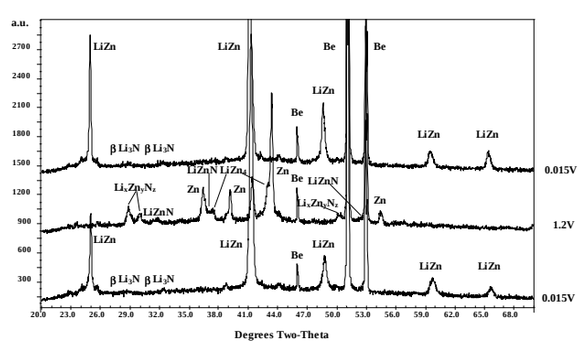

Fig.1: In-Situ XRD patterns of a Zn_3N_2 electrode, at the end of the first and second lithiation at 0.015V and at the end of the first delithiation at 1.2V, showing the reversibility of the transformation reaction of βLi_3N into LiZnN.