Electrochemical Properties of Li-Zn-Al Nanocomposite Materials Prepared by Hydrogen Driven Metallurgical Reactions (HDMR Process)

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It was previously reported that hydrogen driven metallurgical reactions can be used to prepare Li insertion electrodes¹. The following systems were described; LiAlH₄/SnO, LiAlH₄/SiO₂ and LiH/ SnO. In this paper we will report on the LiAlH₄/ZnO system. The HDMR process exploits the effects of the cyclic absorption and desorption of hydrogen structural and metallurgical upon alloy characteristics and the thermodynamic stability of the reactants and reaction products.

The starting materials were powders of $LiAlH_4$ and ZnO obtained from Sigma Corp., St. Louis MO. The synthesis procedure in the present instance is very similar to that previously described. The reaction sequence in this instance is as follows;

$$LiAlH_4 \Rightarrow LiAlH_2 + H_2 \uparrow [1]$$

$$150^{\circ}C$$

$$LiAlH_2 \Rightarrow LiH + Al + 1/2H_2 [2]$$

$$300^{\circ}C$$

Reactions [1] and [2] are known^{2,3}. In a starting mixture having the mol ratio of $3LiAlH_4/ZnO$ we speculate that the following of metathesis reaction [3] and the subsequent reversible disproportionation reaction take place.

$3LiH+3Al+ZnO \Longrightarrow LiZn+Li_2O+3Al+3/2H2 [3]$ $350^{\circ}C$ $LiZn + 1/2 H2 \Leftrightarrow LiH + Zn [4]$ $470^{\circ}C$

The direction of reaction 4 is determined by the hydrogen pressure. Note that 2/3 of the Li content is converted to inert Li₂O. The remaining Li forms a reversible intermetallic compound presumed to be LiZn. The labile hydrogen in reaction [4] was vented into a calibrated volume, measured and corresponded to 100.7% of the total amount present as calculated from the weight of the starting After several compounds. cycles of disproportionation and recombination [4] the reactor was evacuated at 475°C and cooled to

room temperature. We believe that the nanocomposite product is a complex mixture of Li_2O , LiZn and Al, but we have not discounted the presence of LiAl or a reversible Li-Zn-Al ternary alloy. Phase identification is underway.

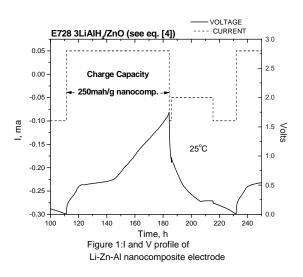
The synthesis reactor was transferred to a drybox, emptied and the product powder was mixed with a carbon binder from which an electrode was prepared as described¹. A test cell containing the nanocomposite electrode and a Li metal counter electrode was assembled and tested using an Arbin Battery Cycler. The results are for the first cycle are summarized in Figure 1.

In addition to the above several other Li-Zn-Al nanocomposite materials of varying Li/Zn ratios were prepared and will be discussed. Overall results confirm our previous assertion that the use of the HDMR process is of great utility for the preparation of a variety of nanocomposite materials.

²J. Block and A. P. Block, Inorg. Chem. *4*, #3, 304 (1965).

³ S. Aronson and F. J. Salzano Inorg. Chem. *8*, *#*7, 1541 (1969).

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¹ J. J. Reilly, J. R. Johnson, G. Adzic, T. Vogt, Y, Zhu and J. Mc Breen, J. Electrochem. Soc. *148*, A636 (2001).