Amorphous Metallic Glass as New High Power and Energy Density Anodes For Lithium Ion Rechargeable Batteries

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ABSTRACT

We have investigated the use of aluminum based *amorphous* metallic glass as the anode in lithium ion rechargeable batteries. Amorphous metallic glasses have no long-range ordered microstructure; the atoms are less closely packed compared to the crystalline alloys of the same compositions; they usually have higher ionic conductivity than crystalline materials, which make rapid lithium diffusion possible. Many metallic systems have higher theoretical capacity for lithium than graphite/carbon; in addition irreversible capacity loss can be avoided in metallic systems. With careful processing, we are able to obtain nano-crystalline phases dispersed in the amorphous metallic glass matrix. These crystalline regions may form the active centers with which lithium reacts. The surrounding matrix can respond very well to the volume changes as these nano-size regions take up lithium. A comparison study of various kinds of anode materials for lithium rechargeable batteries is carried out.

I. INTRODUCTION

The demand for lithium ion rechargeable batteries has been driven by the rapid growth of electronic portable equipment such as cellular phones, laptops and digital cameras etc. In addition, the expectation that rechargeable batteries will play a large role in alternative energy technology and electric vehicles (EV), has made lithium ion rechargeable batteries development into a fast growing area. Although lithium batteries already have the highest energy density of any battery systems, the power and energy requirements of many new portable devices cannot be met with the current choices for electrode materials, especially the negative electrode (anode) materials. Graphite /carbon are used in commercial lithium ion batteries as anodes, nevertheless the capacity of these materials is limited to 340-350 $Ahkg^{-1}$ [1]. Metal alloys have a potential anodic capacity of 1000-2000 $Ahkg^{-1}$ [2]. Industrial interest in metallic alloys has been limited due to their

limited cycle life in commercial cells. This situation changed when Fujifilm announced the development of lithium batteries that were constructed with metal oxide glasses as the anodes [3]. In the first charging step some of the metal oxide is reduced by lithium. The Li_2O produced in this reaction reduces the amount of Li available for cycling in the battery. In this project, we investigate the use of *amorphous* aluminum-based metallic glass as the anode material in lithium ion rechargeable batteries. As these materials contain no oxides, their initial reaction with Li should not reduce the amount of Li for cycling and hence they should keep a more stable capacity than the oxide glasses.

II. BACKGROUND

A battery is an energy storage device. Lithium ion battery is one of the dominant energy storage devices including fuel cell and nickel metal hydride battery. Two-way movement of lithium ions between the

anode and cathode through the electrolyte occurs during charge and discharge processes, as shown in Figure.1.

The first commercial lithium ion rechargeable battery was introduced by Sony Japan in 1989, using graphite as the anode [4]. The reaction mechanism between Li and carbon is an intercalation type reaction [5]. Lithium ions are reversibly stored between layered carbon frameworks. During the reaction, there are no major structural reconfigurations in graphite, which results in a highly reversible reaction. Nevertheless, when graphite is initially charged, the formation of a passivation layer due to electrolyte decomposition at the electrode surface is imminent and results in an irreversible capacity loss [6]. The state-of-art carbon materials also present a safety issue problem [7].
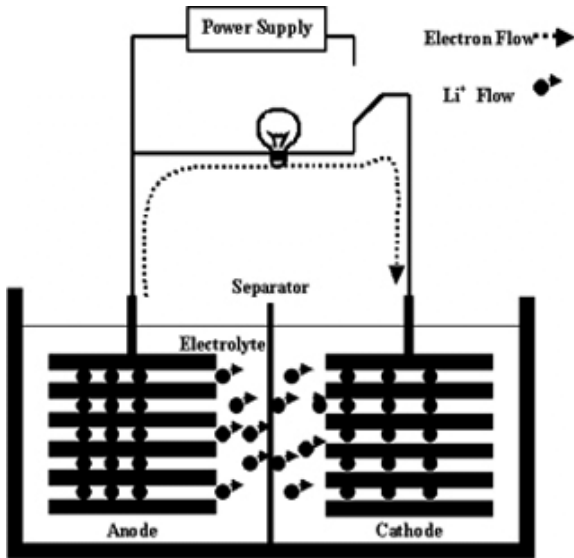

Figure 1. Principle of lithium ion battery - the battery is in discharge state

In 1997, Fujifilm claimed that a high-capacity lithium-storage material in metal-oxide form had been synthesized that could replace the carbon-based lithium intercalation materials currently in extensive use as the anode of lithium-ion rechargeable batteries. This tin-based amorphous composite oxide (TCO) contains Sn(II)-O as the active center for lithium insertion and other glass-forming elements, which make up an oxide network. [3,8] The TCO anode yields a specific capacity for reversible lithium absorption more than 50 percent higher than those of the carbon families. In the first cycle, the Sn-O is reduced by Li, creating a nano-composite of Sn metal dispersed in an oxide matrix. It is this metallic Sn, which provides the capacity to reversibly react with Li. However, the first cycle capacity loss is very high due to the Li consumed in the reduction of Sn-O and formation of Li_2O, which is an irreversible reaction. Since the amount of Li in a practical Li-ion is limited to what is provided by the as-made cathode material, any irreversible Li loss, reduces the cycling capacity of the battery [9].

The search for newer and higher performance anode materials leads to the development of alloy anodes [10]. The utilization of metals and alloys as negative electrode material is based on reversible alloying of lithium with the metal/alloy. Many metals undergo very large volume expansion when alloying with Li and have low Li diffusivities, reducing the applicability of these materials as electrodes. Amorphous metallic glasses have no long-range ordered microstructure; the atoms are less closely packed compared to the crystalline alloys of the same compositions [11]; they usually have higher ionic conductivity than crystalline materials, which make rapid lithium diffusion possible. Many metallic systems have higher theoretical capacity for lithium than graphite/carbon; in addition irreversible capacity loss can be avoided in metallic systems [1]. With careful processing, we are able to obtain nano-crystalline phases dispersed in the amorphous metallic glass matrix. These crystalline regions may form the active centers with which lithium reacts. The surrounding matrix is expected to respond well to the volume changes as these nano-size regions take up lithium.

Three aluminum-based amorphous metallic glass were prepared by rapid solidification. Alloy ingots of compositions $Al_{80}Ni_{10}La_{10}$, $Al_{80}Cu_{10}La_{10}$ and $Al_{88}Ni_9Y_3$ [12] were prepared by arc melting nominal amounts of elements in an argon atmosphere. Melt spinning was carried out in argon atmosphere using a copper wheel with a typical circumferential velocity of 30m/sec. The melt spun ribbons were 20_m thick, 1 to 2mm wide, and up to several meters long. The microstructures of the samples were analyzed using a Philip x-ray diffractometer with a Cu K_ x-ray radiation and a Jeol JEM-100CXII transmission electron microscope (TEM) operating at 100keV. The melt-spun ribbons were ground into powders by mortar and pestle (average particle size > 20_m). Slurries were prepared by mixing the respective powders (85% by weight), carbon black (10% by weight) and polyvinylidene fluoride (PVDF) (5% by weight) in acetone. After drying the mixtures they were conformed into 5mm diameter pellets. Swagelok-type test cells were constructed using these electrodes as the positive electrode; the cells used S&S glass fiber filter paper as the separator, an electrolyte [1M LiPF6 in EC: DMC 1:1 (v/o)] and a lithium foil for the negative electrode. Cells were assembled in an argon-filled glove box, where moisture level is less than 1ppm. All cells were tested with a current density of 0.4mA/cm^2 and were charged and discharged between specified voltage limits.

IV. RESULTS AND DISCUSSION

1. Characterization of Amorphous Metallic Glass

The aluminum based metallic glasses have the following microstructures as shown in the table below. $Al_{80}Ni_{10}La_{10}$ and $Al_{88}Ni_9Y_3$ have better glass forming ability than $Al_{80}Cu_{10}La_{10}$ as shown in the differential scanning calorimetry (DSC) analysis. The DSC result in Figure 2 shows that $Al_{80}Ni_{10}La_{10}$ and $Al_{88}Ni_9Y_3$ have higher crystallization temperatures T_x

and larger enthalpies of crystallization than those of $Al_{80}Cu_{10}La_{10}$.

Table 1. Crystalline phases in the as-spun amorphous metallic glass

	$Al_{80}Ni_{10}La_{10}$	$Al_{80}Cu_{10}La_{10}$	$Al_{88}Ni_9Y_3$
Phase Present	La_3Al_{11} in amorphous matrix	Partially amorphous only	Nano-size _-Al in amorphous matrix
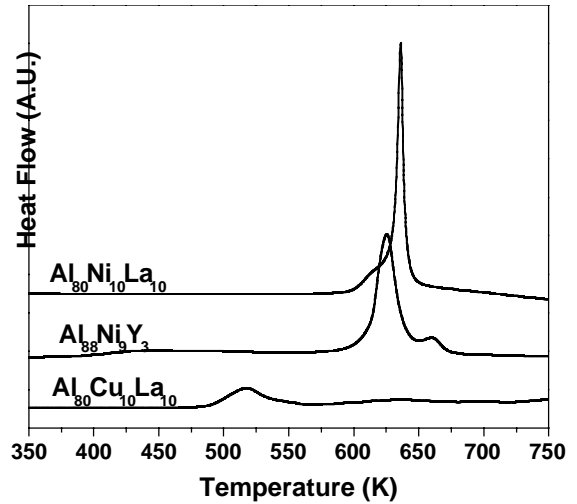
Figure 2. Differential scanning calorimetry result for glassy $Al_{80}Ni_{10}La_{10}$, $Al_{88}Ni_9Y_3$ and $Al_{80}Cu_{10}La_{10}$

The broad maximal in the x-ray diffraction (XRD) spectra of $Al_{80}Ni_{10}La_{10}$ and $Al_{88}Ni_9Y_3$ (Figure 3) indicate large amount of amorphous phase in both samples. Applying Warren's method [13] of particle size measurement, we calculated that the average particle /crystal size in the glass $Al_{88}Ni_9Y_3$ is about 12.6nm.

Transmission electron microscopy was performed to examine the morphology of the crystalline phase and identify the phases. Figure 4 (a) shows that the particle size of the crystalline phase in $Al_{88}Ni_9Y_3$ is indeed in the nano-meter range. The selected area electron diffraction (SAED) pattern shown in Figure 4(b) allows the identification of the crystalline phase as La_3Al_{11}.

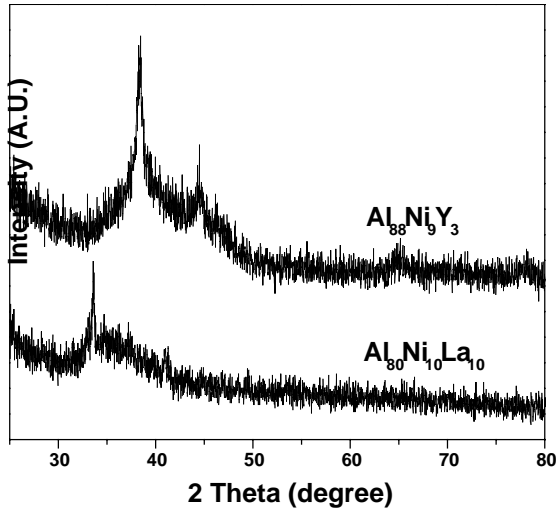Figure 3. X-ray diffraction spectra of as-spun $Al_{80}Ni_{10}La_{10}$ and $Al_{88}Ni_9Y_3$ metallic glass
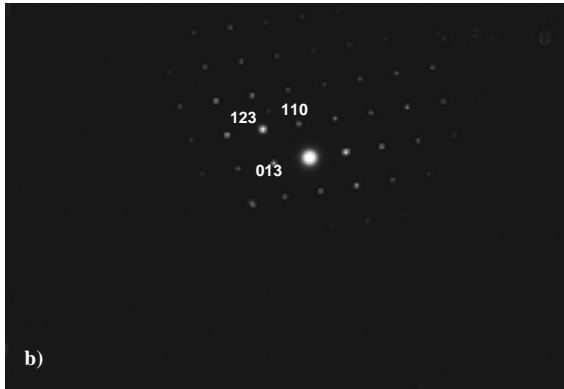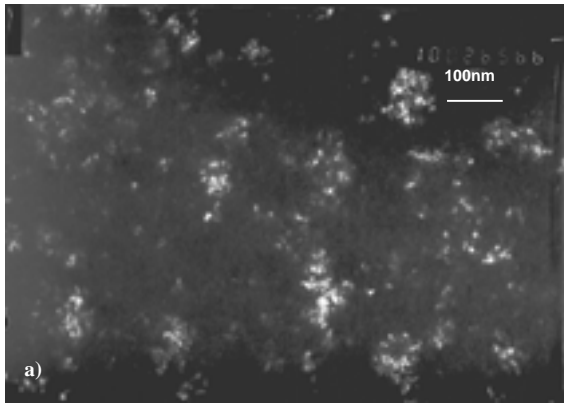

Figure 4. a) Dark-field TEM micrograph of $Al_{88}Ni_9Y_3$, the bright phase is _-Al nano-crystals; b) Diffraction pattern of the crystalline phase in $Al_{80}Ni_{10}La_{10}$, which was identified as La_3Al_{11}.

2. Battery Properties

Figures 5 and 6 show the results from the preliminary electrochemical study of the prepared materials as positive electrodes in lithium cells. A comparison of

aluminum is shown in Figure 5. It can be observed that the lithium insertion voltage of the aluminum based metallic glass is about 0.2volt, lower than that of pure aluminum: V=0.30volt, shown by a plateau shift in the E vs. Time curve. Similar phenomena were observed in Al-Ni-La and Al-Ni-Y metallic glasses.
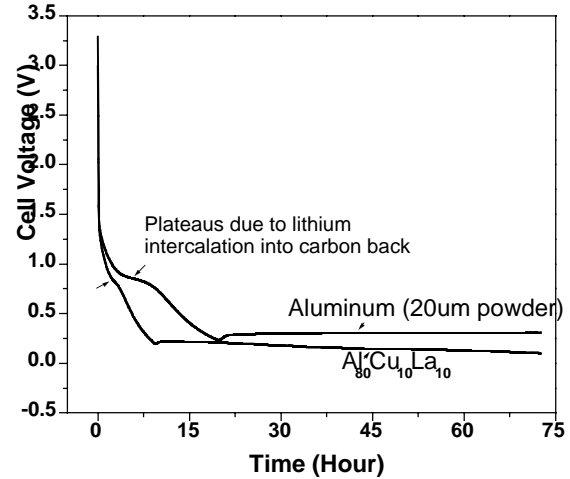

Figure 5. Lithium insertion voltage for crystalline aluminum and glassy $Al_{80}Cu_{10}La_{10}$

Under the applied experimental condition, the charging capacity for Li-ion storage of $Al_{80}Cu_{10}La_{10}$ is 0.45mol lithium per mol of $Al_{80}Cu_{10}La_{10}$ for discharge down to 0V. The Li-ion capacity of $Al_{80}Ni_{10}La_{10}$ is about 0.24mol lithium per mole of $Al_{80}Ni_{10}La_{10}$. The reasons for different capacity, which require further investigation, may have to do with the different phases present in the materials as well as with the grain size of the active material in the electrode.

Figure 6 (a) and (b) show the cycling behaviors of the Li// $Al_{80}Cu_{10}La_{10}$ cells and Li//$Al_{80}Ni_{10}La_{10}$ cells. The first cycle capacity fade is mainly due to the presence of carbon black in the electrode. The subsequent capacity fade is as small as a few percentages.
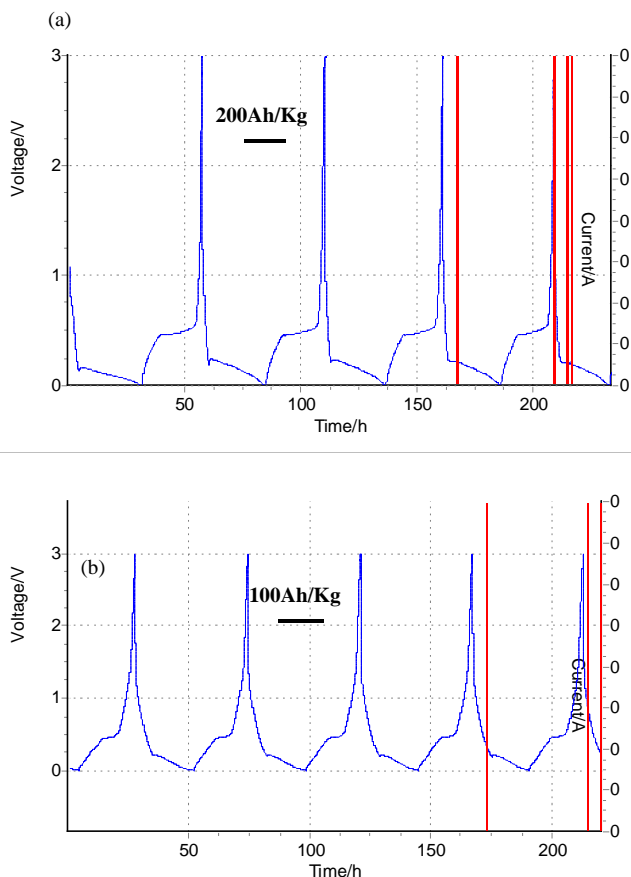
Figure 6. (a) Cycling of electrochemical Li insertion and release on $Al_{80}Cu_{10}La_{10}$ at constant current of 0.08mA per 8.7mg $Al_{80}Cu_{10}La_{10}$, conducted at room temperature between voltage limits of 0V and 3V (C/70); (b) Cycling of electrochemical Li insertion and release on $Al_{80}Ni_{10}La_{10}$ at constant current of 0.04mA per 10.2mg $Al_{80}Ni_{10}La_{10}$, conducted at room temperature between voltage limits of 0V and 3V(C/170).

V. CONCLUSIONS AND FUTURE WORK

In summary, aluminum based amorphous metallic glasses were produced and tested as the anode materials for the lithium ion rechargeable batteries. It was found that the lithium insertion voltages of these metallic glasses were slightly lower than that of crystalline aluminum, which is 0.2Volt. The capacities for these metallic glasses were found lower than the maximum theoretical specific capacity value. However, the compositions and particle size inside the metallic glass anodes have to be optimized before the full lithium capacities of such materials can be confirmed; the particle sizes of the metallic glasses shall be lowered to 10-20_m. The

conformation of the electrode has to be improved as well. Fully amorphous samples will be produced to isolate the capacity of the crystalline phase from the total capacity of the material. In addition, the cycling ability of these anode materials will be investigated.

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