Aluminum alloy anode materials for Li-ion batteries

Z H Sun1,2, Z F Chen1, Q W Fu1 and X Y Jiang1,3,*

1 School of materials and engineering, Tianjin University of Technology, 391 Binshui Xidao, Xiqing District, Tianjin 300384, China
E-mail: 2 sunzhh_977@163.com, 3,* jiangxunyong@tjut.edu.cn

Abstract. Aluminum has larger theoretical capacity of 2235 mAh/g than that of graphite (372 mAh/g), but it has big disadvantages including shorter cycle life and higher irreversible capacity loss. Improving cycle performance can be obtained via alloying of aluminum. In this paper, two ternary aluminum alloy, Al7Cu2Fe and Al73Cu5Fe22 were prepared. The main phase of Al7Cu2Fe alloy was Al7Cu2Fe. The heat treatment increased the proportion of Al7Cu2Fe. The main phase of Al73Cu5Fe22 alloy was Al60Cu30Fe10. The heat treatment reduced the proportion of Al60Cu30Fe10. For two alloys, the heat treatment could increase discharge capacity compared with cast alloy. The discharge capacity was improved by 50%. The content of aluminum in alloys has little effect on improving cycle performance, and it has obvious influence on the phase structure of alloy with heat treatment.

Keywords: aluminum alloy, AlCuFe; anode, lithium storage

1. Introduction

In recent years, lithium-ion batteries (LIBs) have been most important energy devices because of high energy density, high output voltage, long life and low pollution, etc [1]. In order to meet people’s needs for high capacity batteries, looking for a new anode material with great performance becomes research focus [2]. The energy density of LIBs is proportional to the capacity and the operating voltage, thus developing electrode materials with high reversible capacity is one important approach to improve the energy density of LIBs. Aluminum has theoretical capacity of 2235 mAh/g if the Al4Li9 alloy is formed [6], which is much larger than that of graphite (372 mAh/g). Pure aluminum anode has big disadvantages including short cycle life and high irreversible capacity loss because of the large volume expansion during lithiation and delithiation, followed by the loss of electrical contact between individual particles and particles and current collector, resulting in a rapid capacity fade [7]. Improved cycle ability can be obtained by accommodating the volume change via alloying of aluminum. Al-based intermetallic materials (Al2Cu, Fe2Al5) have been studied [10]. The results show that the cycling ability of aluminum alloy anode is improved comparing with pure aluminum electrode.

Here, we report a new aluminum alloy electrode to improve the cycling ability of aluminum anode. The composition of alloy is Al7Cu2Fe and Al73Cu5Fe22. The purpose of addition of third element is to reduce the volume change during the charging and discharging process. To investigate the influence of different microstructure on the capacity of alloy electrode, subsequent heat treatment is applied on the casting alloy powder. The results show that heat treatment can increase the capacity of alloy electrode.

2. Experimental
Al7Cu2Fe and Al73Cu5Fe22 ingot were prepared by arc melting with Fe (chip 99.9%), Cu (shot 99.9%) and Al (shot 99.9%). The ingot were crushed into powder by two routes, 1) One ingot was heat treated at 800 °C in the protection of argon for 12 hours, then cooled down to room temperature. After heat treatment, the alloy was put into ball mill in the ball material ratio 10:1 (stainless steel ball) and proper filling coefficient until the fines were prepared to 300 meshes with molecular sieve. 2) Other ingot was directly milled by mechanical ball milling under the same conditions, without heat treatment. The electrodes for next test were prepared as follow: the alloy powder, the SBR, CMC and acetylene black were mixed with the mass ratios of 85: 2: 3: 10. And then the mixture after a suitable amount of deionized water were stirred with a magnetic whisk for 1 h, and pasted onto the copper foils. The materials were punched into circular electrode slices (15 mm in diameter) after they were dry for 4h at 25 °C. Then the electrode slices were placed on a wild mouthed petri dish to be heated for 10 h at 115 °C in the vacuum drying oven. The average weight of the electrodes was approximately 18 mg. The mental Lithium was used as anode in the cells. And a porous polymeric membrane (Celgard 2400) was used as diaphragm. 1 M LiBF4 dissolved in EC, DEC and EMC mixture of equal volumes was used as electrolyte. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. Charge-discharge cycles of the electrodes were carried out on the NEWARE tester at about 25 °C. The current was carried 100 times at 0.1 C rate. The structure of materials were characterized by X-ray diffraction (XRD, Rigaku D/Max 2500) with Cu Kα radiation in the range of 10°–80°.

3. Results and discussion

3.1. Microstructure and electrochemical characteristics of Al7Cu2Fe

The results of XRD in figure 1(a) show that the main phase of casting Al7Cu2Fe alloy is Al7Cu2Fe. There are small content of Al23CuFe4 and Al60.3Cu30Fe9.7, Al2Cu in the ingot. The multiphase structure comes from the rapid cooling rate during the arc melting process, which makes incomplete peritectic reaction [13]. Heat treatment and mechanical milling only change the proportion of different phase. After mechanical milling and heat treatment, the intensity of diffraction peak on Al2Cu decrease, while the peak on Al7Cu2Fe increase. These may also suggest heat treatment could increase the content of main phase [14].

Figure 1. XRD spectra of alloys (a) Al7Cu2Fe and (b) Al73Cu5Fe22 under different treatment processes, (HT: heat treatment + balling, NHT: ball milling, AM: as cast).

The electrochemical performance of Al7Cu2Fe is studied using the prepared Al7Cu2Fe electrode as working electrode and metallic lithium as the counter electrode. The results are shown in figure 2. Cast
Al7Cu2Fe without heat treatment performed a small discharging platform is about 0.3 V and the charging plateau is about 0.45 V. The charge-discharge cycling of the cells at 0.1 C rate is carried 50 times. It can be seen that the capacity reduce from about 60 mA/h to about 35 mAh/g after first cycle. The capacity of electrode keeps constant. The materials with heat treatment have a higher initial discharge capacity which is double higher than cast electrode. After first cycle, the electrode shows the similar large irreversible capacity as casting alloy, but it shows a better cycling property comparing with casting alloy.

![Figure 2](image1.png)

**Figure 2.** (a) Voltage-capacity of Al7Cu2Fe without heat treatment at first, fifth, tenth cycle, (b) Discharge capacity of Al7Cu2Fe electrodes and change with heat treatment, (HT: heat treatment + balling, NHT: ball milling).

### 3.2. Microstructure and Electrochemical Characteristics of Al73Cu5Fe22

![Figure 3](image2.png)

**Figure 3.** (a) Voltage-capacity of Al73Cu5Fe22 without heat treatment at first, fifth, tenth cycle, (b) Discharge capacity of Al73Cu5Fe22 electrodes and change with heat treatment, (c) Discharge capacity of different alloys without heat treatment, (HT: heat treatment + balling, NHT: ball milling).
Although the content of aluminum in Al$_7$Cu$_2$Fe$_{22}$ is a little higher than Al$_7$Cu$_2$Fe, the main phase of cast Al$_7$Cu$_2$Fe$_{22}$ is Al$_{60}$Cu$_{30}$Fe$_{10}$, which is different from Al$_7$Cu$_2$Fe in Al$_7$Cu$_2$Fe alloy in figure 1 (b). There are some AlCu and a small amount of Al$_{6.35}$Cu$_{2.4}$Fe$_{1.25}$, Al$_{76.8}$Fe$_{24}$, Al$_{23}$CuFe$_4$ and Al$_{13}$Fe$_4$ in the Al$_7$Cu$_2$Fe$_{22}$ alloy. Heat treatment and mechanical milling only change the proportion of main phase. After mechanical milling and heat treatment, the intensity of diffraction peak of Al$_{6.35}$Cu$_{2.4}$Fe$_{1.25}$ and Al$_{76.8}$Fe$_{24}$ increase, instead. This means that the content of main phase of Al$_7$Cu$_3$Fe$_{22}$ decrease with heat treatment.

In figure 3, the electrochemical performance of Al$_7$Cu$_2$Fe$_{22}$ is studied using the prepared Al$_7$Cu$_2$Fe$_{22}$ electrodes as working electrode and metallic lithium as the counter electrode. In figure 3 (a), cast Al$_7$Cu$_2$Fe$_{22}$ doesn’t perform a small discharging platform like Al$_7$Cu$_2$Fe in figure 2(a). The charge-discharge cycling of the cells at 0.1 C rate is carried 50 times. The materials with heat treatment have a higher discharge capacity and a better cycling life than materials without heat treatment in figure 3(b).

The figure 3(c) shows the discharge capacity of two alloys with cycle number. It can be seen that the discharge capacity of two alloys is similar. Although content of aluminum of Al$_7$Cu$_2$Fe is lower than Al$_7$Cu$_2$Fe$_{22}$, its capacity is a little higher than Al$_7$Cu$_2$Fe$_{22}$. The two alloys are composed by different crystalline phase. The main phase of Al$_7$Cu$_2$Fe is Al$_7$Cu$_2$Fe, but the main phase of Al$_7$Cu$_2$Fe$_{22}$ is Al$_{60}$Cu$_{30}$Fe$_{10}$. The excess aluminum in Al$_7$Cu$_2$Fe$_{22}$ precipitates as other phase. This is the reason why Al$_7$Cu$_2$Fe has better capacity than Al$_7$Cu$_3$Fe$_{22}$.

4. Conclusion
Two ternary aluminum alloy, Al$_7$Cu$_2$Fe and Al$_7$Cu$_3$Fe$_{22}$ have been prepared, and the lithium storage property of two alloys studied. The experimental results show that: the main phase of cast Al$_7$Cu$_2$Fe is Al$_7$Cu$_2$Fe. The heat treatment increase the proportion of Al$_7$Cu$_2$Fe. The main phase of cast Al$_7$Cu$_2$Fe$_{22}$ is Al$_{60}$Cu$_{30}$Fe$_{10}$. The heat treatment reduces the proportion of Al$_{60}$Cu$_{30}$Fe$_{10}$. For two alloys, the heat treatment can increase discharge capacity comparing with cast alloys. The discharge capacity is improved by 50%. The content of aluminum in alloys has little effect on improving cycle performance.

References
[1] Zhang W J 2011 A review of the electrochemical performance of alloy anodes for lithium-ion batteries Journal of Power Sources 196 13–24
[2] Winter M, Besenhard J O and Spahr M E 1998 Insertion electrode materials for rechargeable lithium batteries Advanced Materials 10 725–763
[3] Larcher D, Edstroem K, Beattie S and Larcher D 2007 Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries J. Mater. Chem. 17 3759–3772
[4] Thackeray M M, Vaughney J T and Fransson L M L 2002 Recent developments in anode materials for lithium batteries JOM, 54 20–23
[5] Wachtler M, Winter M and Besenhard J O 2002 Anodic materials for rechargeable Li-batteries Journal of Power Sources 105 151–160
[6] Gayle F W, Sande J B V and Mcalister A J 1984 The Al-Li (aluminum-lithium) system Journal of Phase Equilibria 5 21
[7] Liu Y et al. 2011 In situ transmission electron microscopy observation of pulverization of aluminum nanowires and evolution of the thin surface Al$_2$O$_3$ layers during lithiation-delithiation cycles Nano Letters 11 4188–4194
[8] Kasavajjula U, Wang C and Appleby A J 2007 Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells Journal of Power Sources 163 1003–1039
[9] Winter M, Brodd R J 2004 What are Batteries, fuel Cells and supercapacitors? ChemInform, 104 4245–69
[10] Lindsay M J, Wang G X and Liu H K 2003 Al-based anode materials for Li-ion batteries Journal of Power Sources 119 84–87
[11] Su Y C, Yan J and Lu P T 2006 Thermodynamic analysis and experimental research on Li
intercalation reactions of the intermetallic compound Al₂Cu. Solid State Ionics 177, 507–513

[12] Hamon Y, Brousse T and Jousse F 2001 Aluminum negative electrode in lithium ion batteries. Journal of Power Sources 97–98, 185–187

[13] Jian X et al. 2003 Study on NiSb₂ as a new lithium-ions batteries anode material. Rare Metal Materials & Engineering 32, 283–286

[14] Wang Y F and Zhuang X W 1992 Amorphous materials and their application (Beijing, China: Higher Education Press) pp 21–30