

Al-based anode materials for Li-ion batteries

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Abstract

The electrochemical performance of Fe_2Al_5 was investigated as an anode material for lithium-ion batteries. Fe_2Al_5 was prepared by arc melting the constituent elements, crushing to a suitable size and then ball milling. By removing samples from the ball mill at various times the effect of milling time on the electrochemical properties was examined. The highest discharge capacity (485 mAh/g) observed was as a result of ball milling for 10,000 min which is consistent with the theoretical capacity for formation of AlLi (543 mAh/g). Cyclic voltammetry and differential capacity plots, however, do not offer conclusive evidence of the formation of AlLi . Both charge and discharge capacity improved with increasing milling but cycle life remained poor. Removal of lithium from the structure was difficult with charge capacities being quite low. The first charge capacities for instance were in the range of 20–40% of the first discharge capacity.

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1. Introduction

In recent years, intermetallic materials have been investigated as possible anode materials for lithium-ion batteries. This work has predominantly concentrated on the use of tin as an active material combined with any one of a large number of inactive materials [1–3]. Tin is not the only material that is active towards lithium. Other materials include aluminium, silicon and magnesium [4,5]. Examination of the Al–Li binary alloy phase diagram shows that aluminium can form three alloys with lithium [6]. The theoretical mass capacities (Table 1) of these alloys show that the formation of even AlLi phase has the same theoretical capacity (993 mAh/g) as the most lithium rich Sn–Li phase ($\text{Li}_{22}\text{Sn}_5$). Formation of Al_4Li_9 (2235 mAh/g) has been reported [7]. Given that Fe_2Al_5 is 55 wt.% aluminium the theoretical discharge capacity for full reaction of aluminium in the intermetallic is 543 mAh/g for formation of AlLi and 1223 mAh/g for formation of Al_4Li_9 .

Another area where aluminium offers a potential benefit over tin is the expansion due to the alloying reaction. Full reaction of metallic tin with lithium to form $\text{Li}_{22}\text{Sn}_5$ results in a 676% increase in volume, whilst the corresponding increase for the reaction of metallic aluminium to form LiAl is only 97% [8]. Previous investigations of aluminium-based

intermetallic materials (Al_2Cu , Al_6Mn , Al_4Mn) have however reported inactivity of these materials with the small reversible capacity being attributed to the carbon content of the electrode [9].

The potential use of aluminium-based intermetallics as anodes for lithium-ion batteries is investigated through the use of Fe_2Al_5 .

2. Experimental

Fe (chip 99.98%, Aldrich) and Al (shot 99.9%, Aldrich) were combined in the atomic ratio of 1:3. Using an arc melting system the Fe and Al were melted together and the resulting alloy slug was crushed until the fines passed through a 150 μm sieve. The material was then ball milled in a planetary ball mill (Pulverisette-5) at 90 rpm in a steel milling vessel with 80 mm internal diameter and approximate volume of 200 cm^3 . Stainless steel balls of 5 mm diameter were utilized and ethanol added as a process control agent to the level of the top of the balls. The ratio of balls to powder was approximately 20:1 (8.852 g powder:173 g balls). Small quantities of powder were removed at a number of intervals to allow for X-ray diffraction (XRD) and fabrication of electrodes for electrochemical testing. Powder was removed at total milling times of 100, 500, 2000, and 10,000 min with ethanol being added at these intervals if required. XRD was carried out using a Phillips

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Table 1
Summary of Al–Li binary phases and their theoretical mass capacities

Phase	Theoretical mass capacity (mAh/g)
AlLi	993
Al ₂ Li ₃	1490
Al ₄ Li ₉	2235

PW1730 diffractometer with Cu K α radiation using an accelerating voltage of 40 kV and current of 20 mA. Powder samples and electrodes fabricated from such samples will be referred to according to their ball milling time in minutes with a prefix of BM.

Electrodes were fabricated on copper substrates of approximately 1 cm diameter and featured a loading of approximately 14 mg for BM0, 5 mg for BM100 and 1 mg for the remaining samples. The BM0, BM100 and BM500 electrodes contained no conductivity additive, whilst the BM2000 and BM10,000 electrodes contained approximately 10 wt.% conductivity additive (Vulcan XC-72). The slurry to produce the electrodes was made with the addition of a 5 wt.% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solution. Finished electrodes consisted of 85–95 wt.% powder, 10–0 wt.% conductivity additive and 5 wt.% PVDF. Electrodes were dried overnight at 120 °C before being pressed and placed into a glove box (Mbraun, Unilab, Germany) prior to assembly in custom test cells. The test cells consist of a Teflon case, which has been threaded to accept two stainless steel bolts as the terminals of the cell and a small stainless steel spring. The threads of the bolts are wrapped with Teflon tape and once the cell is assembled dental wax is melted around the bolt heads to complete the sealing of the cell to the atmosphere. Three electrode test cells were also used and have the same construction with the addition of a small stainless steel bolt threaded into an additional hole in the Teflon case. The end of the bolt is covered with lithium to act as a lithium reference electrode. The electrolyte (Merck, Germany) used during cell assembly was 1 M LiPF₆ in a 1:1 mixture by volume of ethylene carbonate (EC) and dimethyl carbonate (DMC). Galvanostatic charge/discharge was carried out with a current of 50 μ A.

3. Results and discussion

3.1. Structural and microstructural characterization of Fe₂Al₅

XRD showed the material to be Fe₂Al₅ (orthorhombic) with peak broadening evident with increase of milling time (Fig. 1). The structure remained well defined up to a milling time of 500 min whilst on further milling (2000 and 10,000 min) the scans indicate an X-ray amorphous structure. FWHM were determined for the (1 1 1) (0 2 0) peak using Traces [10]. The crystalline size (d) was then estimated after subtracting instrumental error ($\beta_{\text{sam}}^2 = \beta_{\text{exp}}^2 - \beta_{\text{inst}}^2$)

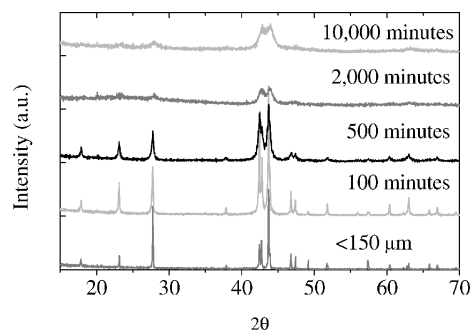


Fig. 1. XRD of Fe₂Al₅ powders and change with ball milling time.

using the Scherrer equation ($d = 0.9\lambda/\beta \cos \theta$) as 72 nm for BM100 and 41 nm for BM500. These crystallite sizes are well above the minimum reported crystallite sizes for mechanical milling of aluminium (20–24 nm) and iron (8 nm) compiled by Koch [11] and the 10 nm crystallite size reported in the investigation of Al₂Cu, Al₆Mn, Al₄Mn [9].

SEM was used to determine the effect of milling on the particle size of the powders (Fig. 2). Examination of micrographs showed a decrease in the observed maximum particle size from 100 μ m for BM0 to 0.5 μ m for BM10,000 (Table 2). The particle sizes for the BM100, BM500 and BM2000 are also in the range of particle sizes reported in the previous investigation of Al₂Cu (1–10 μ m) [9].

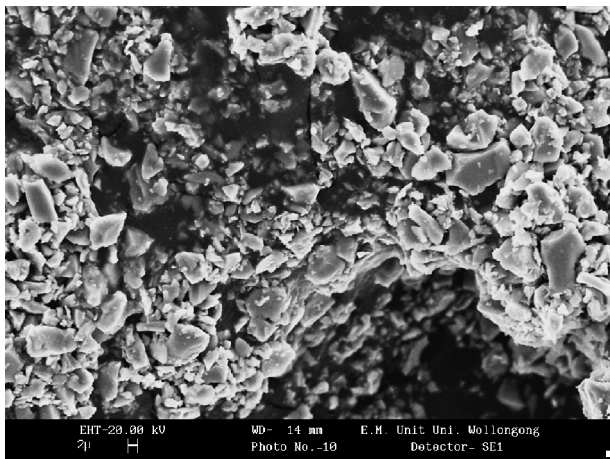
3.2. Electrochemical characteristics of Fe₂Al₅

The electrochemical performance of Fe₂Al₅ was evaluated using the prepared Fe₂Al₅ electrodes as a working electrode and metallic lithium as the counter electrode. The first discharge of Fe₂Al₅ electrodes (Fig. 3) demonstrates a clear increase in discharge capacity with increasing milling time (reduction in particle size). Particle size has also been shown to have a dramatic effect on the electrochemical performance of metallic tin [12] and tin-based [13] electrodes. The BM10,000 electrodes first discharge capacity of 485 mAh/g compares favourably to the theoretical discharge capacity for formation of AlLi (543 mAh/g). Whilst the first discharge of BM500 electrode (52 mAh/g) and its reversible capacity of approximately 20 mAh/g demonstrate that crystalline Fe₂Al₅ has some activity towards lithium unlike Al₂Cu, Al₆Mn, Al₄Mn where the reversible capacity of approximately 20 mAh/g was attributed to the carbon content

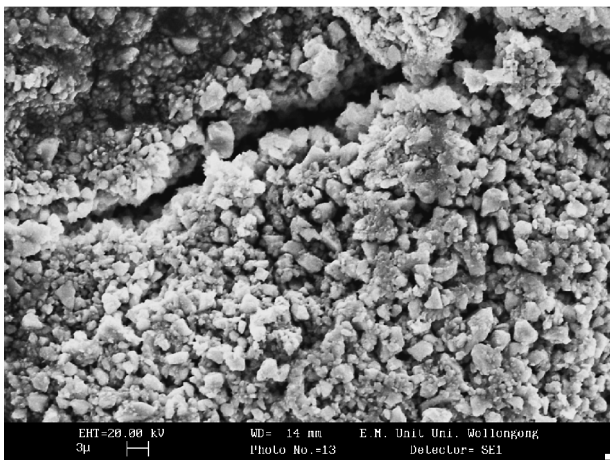
Table 2
Maximum particle size observed during SEM observation of samples

Sample	Maximum particle size ^a (μ m)
BM0	100
BM100	10
BM500	3
BM2000	1
BM10000	0.5

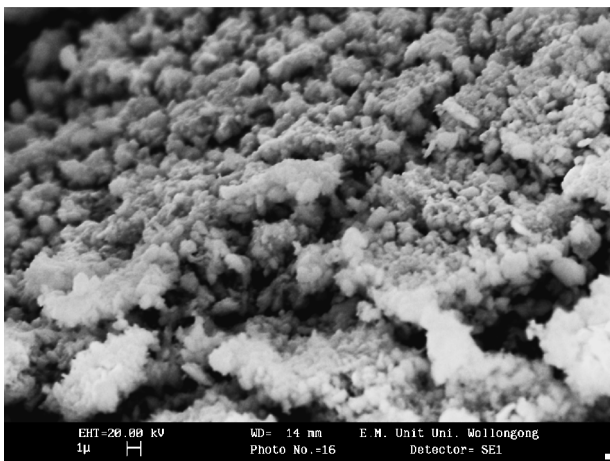
^a Observed particle size from SEM micrographs.



(a)



(b)



(c)

Fig. 2. SEM micrographs of selected ball milled powder samples: (a) 100 min, (b) 500 min, (c) 2000 min.

of the electrode [9]. Unfortunately, the discharge capacity drops dramatically after the first discharge in all cases (Fig. 4).

Examination of the first charge capacities (Fig. 5) of the various samples indicates lithium is not easily extracted

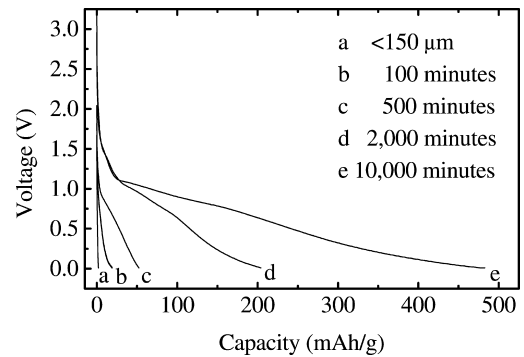


Fig. 3. First discharge of Fe_2Al_5 electrodes and change with ball milling time.

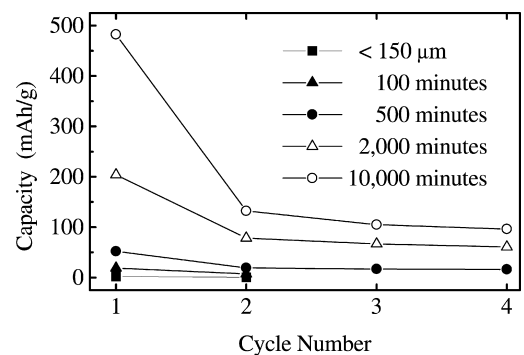


Fig. 4. Discharge capacity of Fe_2Al_5 electrodes and change with ball milling time.

from the structure. As a result subsequent discharge capacities are much lower than the first discharge capacity. For BM10,000 the second discharge capacity is approximately 30% of the initial discharge capacity, whilst for the other samples it is approximately 40%. As a result of ball milling the charge and discharge capacities increase dramatically. This is particularly evident for milling times greater than 100 min (Fig. 6). The first discharge capacity increases more rapidly with milling time than that of the first charge and second discharge. The irreversible capacity may be able to

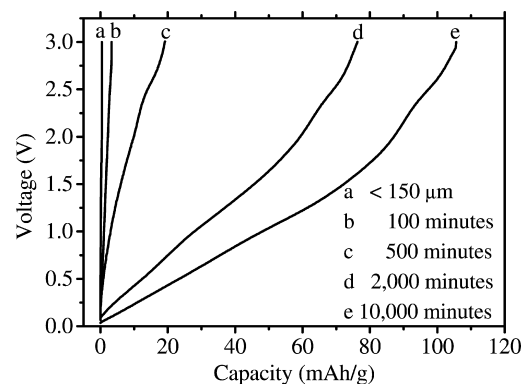


Fig. 5. First charge of Fe_2Al_5 electrodes and change with ball milling time.

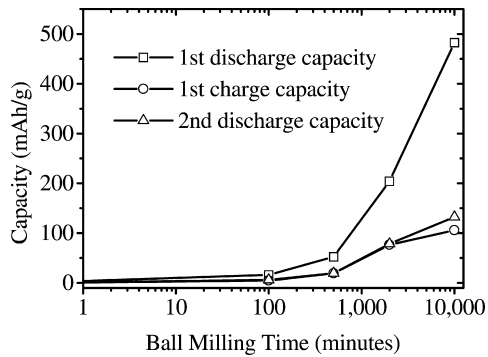


Fig. 6. Variation of capacity with ball milling time.

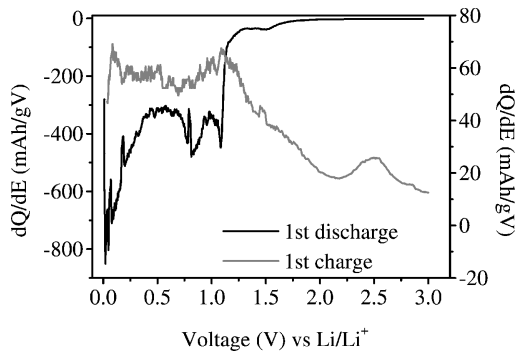


Fig. 7. Differential capacity plots of first charge and discharge of ball milled 10,000 min electrode.

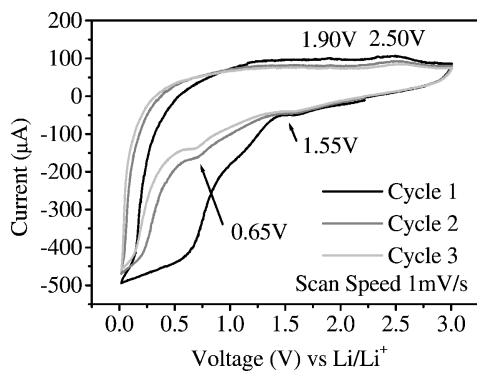


Fig. 8. Cyclic voltammetry of ball milled 10,000 min electrode.

be improved with suitable modification of the microstructure through further ball milling and/or annealing operations.

Although the first discharge capacity of BM10,000 is consistent with the theoretical discharge capacity of the alloy for formation of AlLi, differential capacity plots of the first charge and discharge (Fig. 7) and cyclic voltammetry (Fig. 8) indicate that other reactions are occurring and that the reaction $\text{Al} + \text{Li} \rightarrow \text{AlLi}$ may not be occurring. Cyclic voltammetry of aluminium thin films indicate reactions at approximately 0.2 V on discharge and 0.45 V on charging [14]. Cyclic voltammetry clearly indicates little

reaction occurs during charging but the $\text{Al} + \text{Li} \rightarrow \text{AlLi}$ reaction may be occurring on discharge.

4. Conclusion

The electrochemical performance of Fe_2Al_5 is improved significantly via ball milling but not to a sufficient degree as yet to be a viable replacement to existing anode materials. If the difficulty in removing lithium from the structure can be overcome Fe_2Al_5 may be a suitable anode material for lithium-ion batteries. Altering the microstructure by further milling and/or annealing operations may be able to improve the electrochemical performance of the alloy. Crystalline Fe_2Al_5 electrodes that contained no conductive additive clearly demonstrated that some interaction with lithium occurs, with the ball milled 500 min electrode having a reversible capacity of approximately 20 mAh/g. Despite the crystalline size of 41 nm (BM500) being greater than the 10 nm of previous aluminium intermetallics investigated and reported as inactive [9], though the particle sizes were comparable.

There is uncertainty over the reaction mechanism though. The first discharge capacity of ball milled 10,000 min electrodes (485 mAh/g) is consistent with the theoretical discharge capacity of Fe_2Al_5 for the formation of AlLi (543 mAh/g). However, cyclic voltammetry and differential capacity plots suggest that other reactions are occurring and do not offer conclusive proof that the reaction $\text{Al} + \text{Li} \rightarrow \text{AlLi}$ occurs.

References

- [1] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, J. Power Sources 81–82 (1999) 383–387.
- [2] H. Kim, Y.-J. Kim, D.G. Kim, H.-J. Sohn, T. Kang, Solid State Ionics 144 (2001) 41–49.
- [3] M. Wachtler, M. Winter, J.O. Besenhard, J. Power Sources 105 (2002) 151–160.
- [4] G.X. Wang, L. Sun, D.H. Bradhurst, S. Zhong, S.X. Dou, H.K. Liu, J. Alloys Compd. 306 (2000) 249–252.
- [5] Z. Shi, M. Liu, D. Naik, J.L. Gole, J. Power Sources 92 (2001) 70–80.
- [6] H. Baker (Ed.), ASM Handbook—Alloy Phase Diagrams, ASM International, Materials Park, 1992, pp. 2–47.
- [7] A.V. Trifonova, A.A. Momchilov, B.L. Puresheva, I. Abrahams, Solid State Ionics 143 (2001) 319–328.
- [8] J.O. Besenhard, M. Hess, P. Komenda, Solid State Ionics 40–41 (1990) 525–529.
- [9] D. Larcher, L.Y. Beaulieu, O. Mao, A.E. George, J.R. Dahn, J. Electrochem. Soc. 147 (2000) 1703–1708.
- [10] Diffraction Technology Ltd., Traces 5.1.0, Diffraction Technology Pty. Ltd., Australia, 1999.
- [11] C.C. Koch, Nanostruct. Mater. 9 (1997) 13–22.
- [12] J. Yang, Y. Takeda, N. Imanishi, T. Ichikawa, O. Yamamoto, J. Power Sources 79 (1999) 220–224.
- [13] J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1997) 87–90.
- [14] Y. Hamon, T. Brousse, F. Jousse, P. Topart, P. Buvat, D.M. Schleich, J. Power Sources 97–98 (2001) 185–187.