

Expanded metal a novel anode for Li-ion polymer batteries

K. Zaghbi^{a,*}, M. Gauthier^b, M. Armand^b

^a*Institut de Recherche d'Hydro-Québec (IREQ), Service Chimie des Matériaux, 1800 boul. Lionel-Boulet, Varennes, Que., Canada J3X 1S1*

^b*International Joint Laboratory CNRS-UdM (UMR 2289), Department of Chemistry, University of Montreal, 2900 Edouard Montpetit C.P. 6128 Succ. Centre Ville, Montreal, Que., Canada QC H3C 3J7*

Abstract

An electrochemical cell using an electrode of expanded metal (EXMET[®]) is demonstrated. The sheet of EXMET[®] contains voids with open volume and geometric arrangement that are capable of locally absorbing any lateral expansion. Consequently, all cumulative changes in the plane of the EXMET[®], when an Li–Al alloy is initially formed, are avoided. Three configurations of electrochemical generators utilizing cathodes of V₂O₅, FePO₄ and LiCoO₂ are described. Studies of alloy and dense anode sheets with local stress relaxation were demonstrated by in situ optical microscopy (OM) and scanning electron microscopy (SEM) using expanded metal. These studies indicate that a dense anode offers advantages for application in SPE-cells, including safety, long life and reliability.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Lithium alloy; Expanded metal; Li-ion polymer; V₂O₅; FePO₄; LiCoO₂ ARC; Safety

1. Introduction

The use of alloys of alkali metals such as lithium has been proposed and demonstrated with success in electrochemical cells containing molten-salt electrolytes [1,2]. In an organic electrolyte, and more particularly with a polymer electrolyte, which has a thickness less than 100 μm thick, it becomes very difficult to operate with anodes in the form of alloy sheets. Indeed, intermetallic compounds of lithium (e.g. LiAl, Li₂₁Si₅, Li₂₂Pb₅, etc.) that can be used as anodes are hard and brittle and cannot be laminated. This is also the case for lithium or weakly alloyed lithium. The expansion of the host metal in the plane of the electrode is accommodated along its entire surface and creates folds that relieve the local stresses generated by expansion. The consequence is that short circuits are formed between the electrodes or that mechanical defects are produced, which are detrimental to the operation of a cell. In this paper, we use an expanded metal, which has voids with open volume and geometric arrangement that are capable of locally absorbing any lateral expansion. Consequently, all cumulative mechanical changes when an alloy is initially formed in the plane of the EXMET[®] sheet are avoided.

The aim of this paper is to demonstrate the viability of electrodes using expanded metal and dense anode sheets with local stress relaxation. More particularly, an electrochemical cell that contains a negative electrode such as aluminum in three different cell chemistries was investigated. Observations of mechanical changes in the expanded metal by in situ optical microscopy (OM) and in situ scanning electron microscopy (SEM) are presented.

2. Experimental

Two methods are used to study the volume expansion of Al metal and Al expanded metal in contact with Li. The first method illustrated in Fig. 1, shows a vertical cross-section view of an experimental device for in situ optical microscopy observations of alloy formation from a Li sheet and a host structure of Al. The second method illustrated in Fig. 2, shows an experimental device for in situ SEM observations of alloy formation; this method was described elsewhere [3].

The initial cell chemistries are based on three cell configurations (see Fig. 3).

- Type I: Al collector/(V₂O₅ or FePO₄)/SPE/Li^o/C/EXMET[®] (Al).
- Type II: Al collector/(V₂O₅ or FePO₄)/SPE/EXMET[®] (Al)/C/Li^o.
- Type III: Al collector/LiCoO₂/SPE/C/EXMET[®] (Al).

* Corresponding author. Tel.: +1-450-652-8019; fax: +1-450-652-8424.
E-mail address: karimz@ireq.ca (K. Zaghbi).

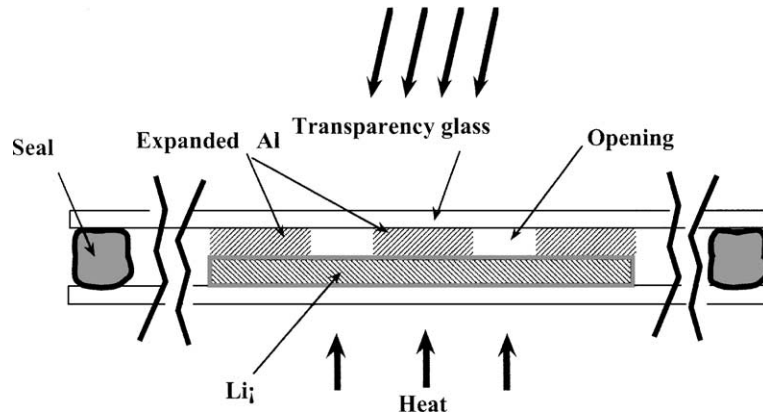


Fig. 1. Vertical cross-section view of an experimental device for in situ optical observations of alloy formation between Li and a host structure of expanded Al.

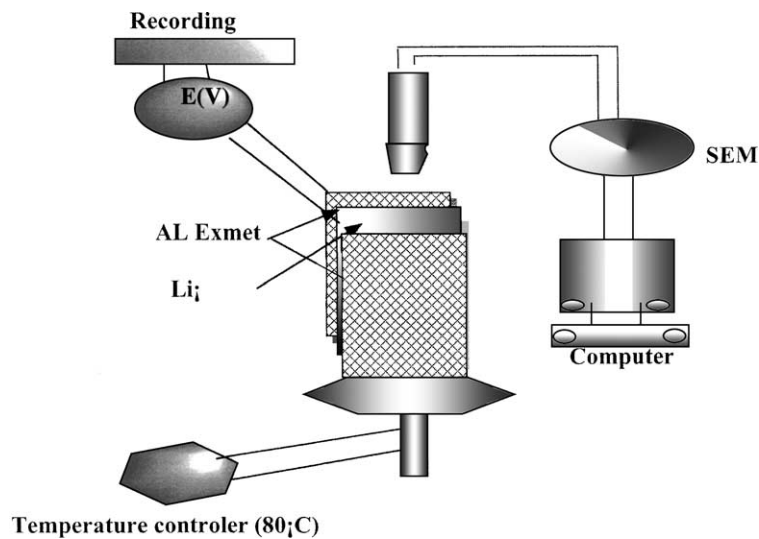


Fig. 2. General view of an experimental device for in situ SEM observations of alloy formation between Li and a host structure of expanded Al [3].

SPE represents the solid polymer electrolyte consisting of a mixture PEO and LiTFSI salt [3], and C designates a thin film of carbon, which is dispersed in a bonding polymer electrolyte. This composite is an electrochemical bridge (ionic and electronic conductor). EXMET[®] (Al) is a sheet of expanded metal that is commercially produced (EXMET[®], Naugatuck, CT, USA). Accelerated Rate Calorimetry (Columbia Scientific, Austin, TX, USA), commonly known as ARC, was used to study the safety of the cell chemistries. In this technique, the temperature of the sample is systematically increased to higher temperatures until a spontaneous thermal event produces additional heat (stabilization of the temporary rise in temperature). This is a sensitive technique that is known to detect localized exothermic reactions, which can present a danger under abusive use conditions. Charge–discharge cycling and slow cyclic voltammetry of these cells were carried out using galvanostatic and potentiostatic methods (Macpile[®], Claix, France). All experiments were conducted at 60, 70 and 80 °C.

3. Discussion of results

3.1. In situ OM and SEM

Fig. 4 shows the performance of 20 μm thick Al sheet in contact with metallic Li that is 18 μm thick. The contacting sheets are compressed with the device shown in Fig. 1. After heating at 80 °C for 1 h, the Li sheet dissolved by reaction with Al. In addition, Al forms a plurality of folds that protrude from the plane of the sheets because of lateral expansion resulting from alloy formation. In a complete cell with polymer electrolyte, this phenomenon generally results in a short circuit. The results in Fig. 5 were obtained by replacing the dense Al sheet with a sheet of expanded metal (25 μm thick after compressing, 50% void volume, openings were about 145 μm across). To facilitate complete alloy reaction between Li and Al, the latter was covered with a thin film of composite C. The results in Fig. 5 indicate that the proportion of the openings is too high to permit complete closure of the alloy structure after reaction. The details of the host structure

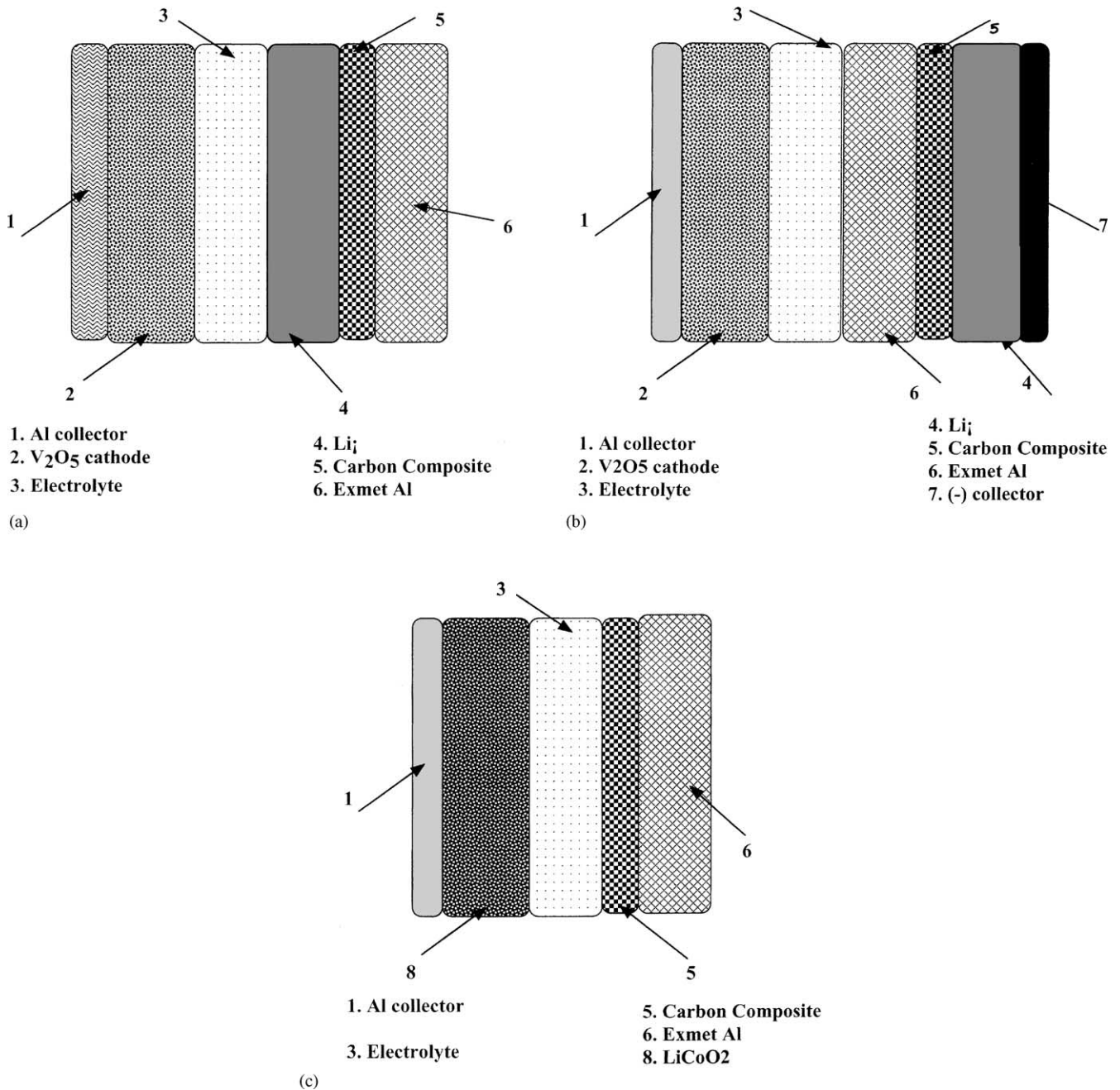


Fig. 3. (a) Schematic illustration of Type I cell: Al collector/ $(V_2O_5$ or $FePO_4$)/SPE/ Li^+ /C/EXMET[®] (Al); (b) schematic illustration of Type II cell: Al collector/ $(V_2O_5$ or $FePO_4$)/SPE/EXMET[®] (Al)/C/ Li^+ and (c) schematic illustration of Type III: Al collector/ $LiCoO_2$ /SPE/C/EXMET[®] (Al).

after chemical reaction with Li can be seen. Furthermore, it is apparent that no channels were formed during reaction, contrary to the case of Fig. 4 which indicates the Al sheet cannot alleviate volume and stress. The expanded metal remains perfectly flat, which is an essential condition for good operation of a polymer–electrolyte cell with thin film components.

Another surprising result obtained with in situ electronic microscopy was that alloy formation in the mesh of the open structure produces a lateral expansion of the dense part, which is smaller than expected from the values in Table 1 [4].

The observed expansion is about 10%, while the expected value from Table 1 is 94%. This phenomenon results from the directional nature of the source of lithium, which permits insertion, and from the solid nature of the device, which has been produced. These observations suggest that an optimized structure of Al (EXMET[®]) should have a void volume in the order of 20%.

Fig. 6 shows the mechanism for chemically operating a “dense” alloy negative electrode with local stress relaxation. Fig. 6a shows the sequence for the formation of the alloy sheet; and Fig. 6b shows the behavior in cross-section

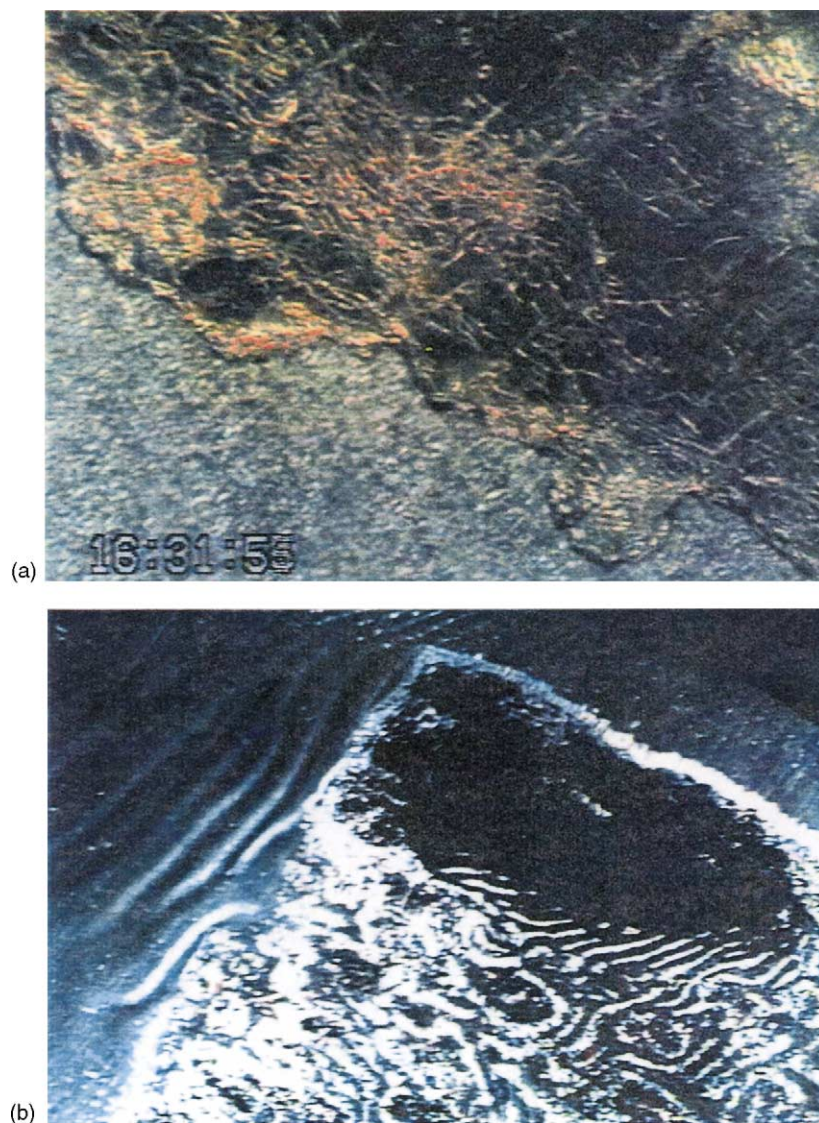


Fig. 4. (a) Representation of an Al sheet (full surface) and Li sheet that are mechanically compressed by the device illustrated in Fig. 1; pressure applied before alloy formation; (b) representation of (a) after alloy formation and the disappearance of Li by chemical reaction at 80 °C.

Table 1
Calculated volumetric expansion of different alloys [4]

Non-fusible anodes						
Before			After			
Discharged anodes	cm ³ /Ah	cm ³ /C (×10 ⁻⁴)	Charged anodes	cm ³ /Ah	cm ³ /C (×10 ⁻⁴)	Variation (cm ³ /Ah)
Li	0.49	1.36	Li	0.49	1.36	0
C	1.19	3.32	LiC ₆	1.47	4.09	23
Si	0.11	0.30	Li ₂₁ Si ₅	0.44	1.22	309
As	0.16	0.45	Li ₃ As	0.49	1.36	201
Al	0.37	1.04	LiAl	0.72	2.01	94
Sn	0.14	0.40	Li ₂₁ Sn ₅	0.51	1.43	257
Sb	0.23	0.63	Li ₃ Sb	0.56	1.55	147
Pb	0.15	0.43	Li ₂₁ Pb ₅	0.52	1.44	237

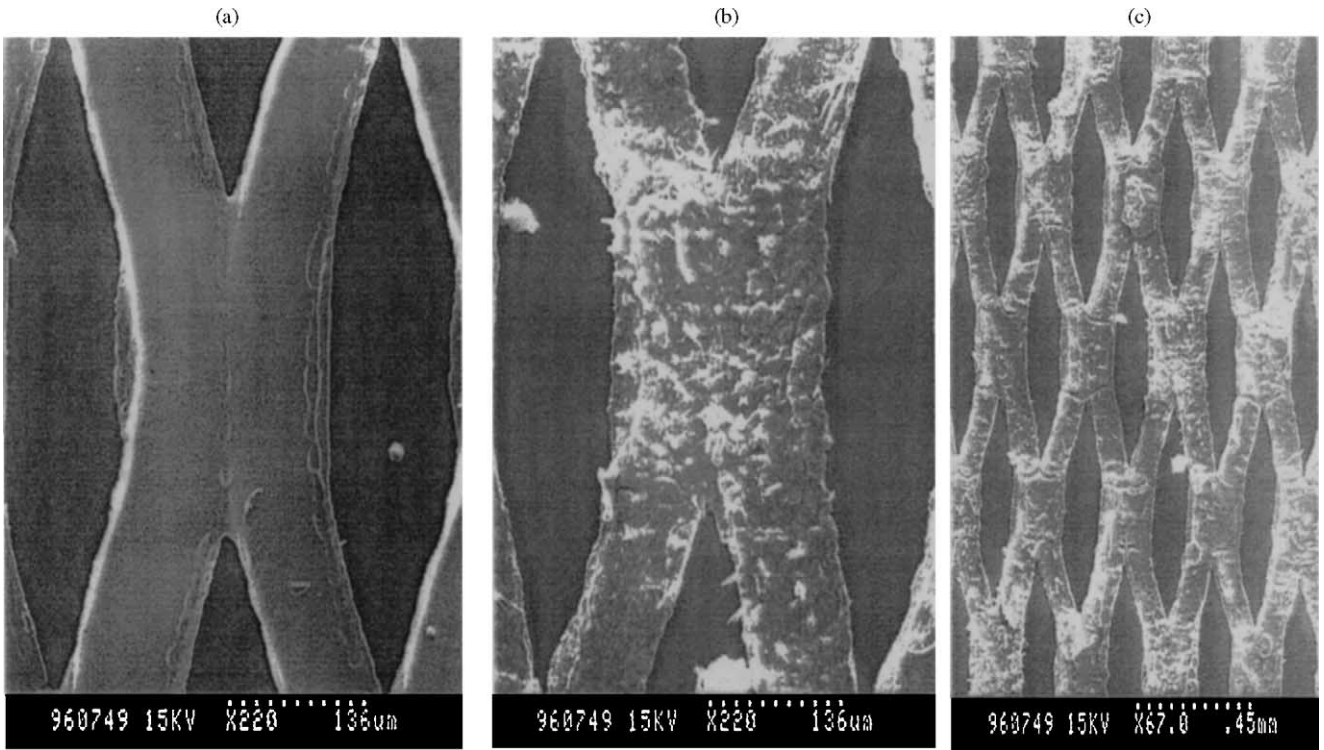


Fig. 5. (a) Micrograph from scanning electron microscopy (scale, 220×) of EXMET[®] expanded Al. (b) Micrograph from scanning electron microscopy showing the details of EXMET[®] expanded Al sheet with a Li sheet at 80 °C in a device illustrated in Fig. 2. (c) Micrograph from scanning electron microscopy of the same sheet as illustrated in (b), except at a lower magnification to show that no folds or grooves are formed.

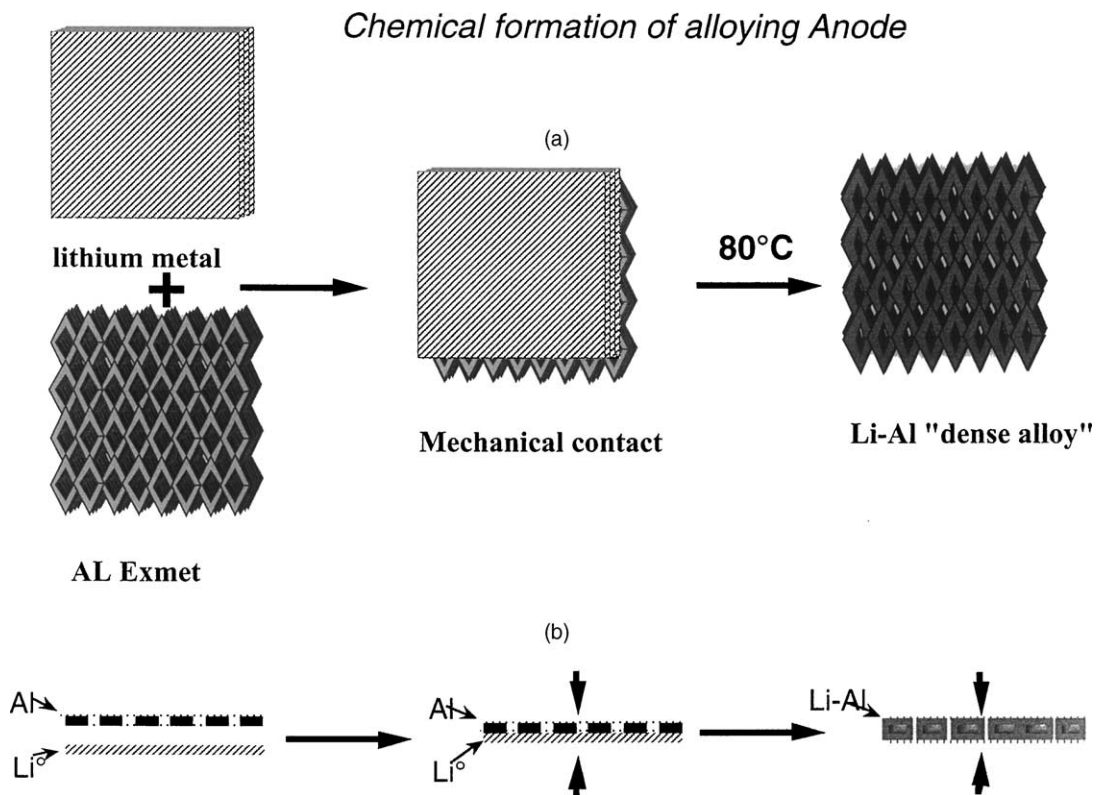


Fig. 6. (a) Schematic illustration of the formation of an alloy electrode (anode dense) and (b) cross-section view of the illustration represented in Fig. 2.

of the expanded sheet during alloy formation. In this case, pressure is maintained on the sheets of EXMET[®] and Li to ensure there is good interfacial contact and to prevent deformation of the surface of the sheets.

3.2. Electrochemical study

3.2.1. Type I

The performance of the cell in Fig. 3a (Type I) is compared to an equivalent cell in which the anode is a

sheet of Li. The cathode material is V_2O_5 . The initial discharge curves are compared in Fig. 7a where it can be observed that the performance is similar but the average voltage is lower. This voltage decrease corresponds to the lower activity of Li in the Li–Al alloy, i.e. between about +270 and +420 mV versus Li° .

3.2.2. Type II

This cell includes the elements of Type I except that the position of the EXMET[®] and film of carbon composite is

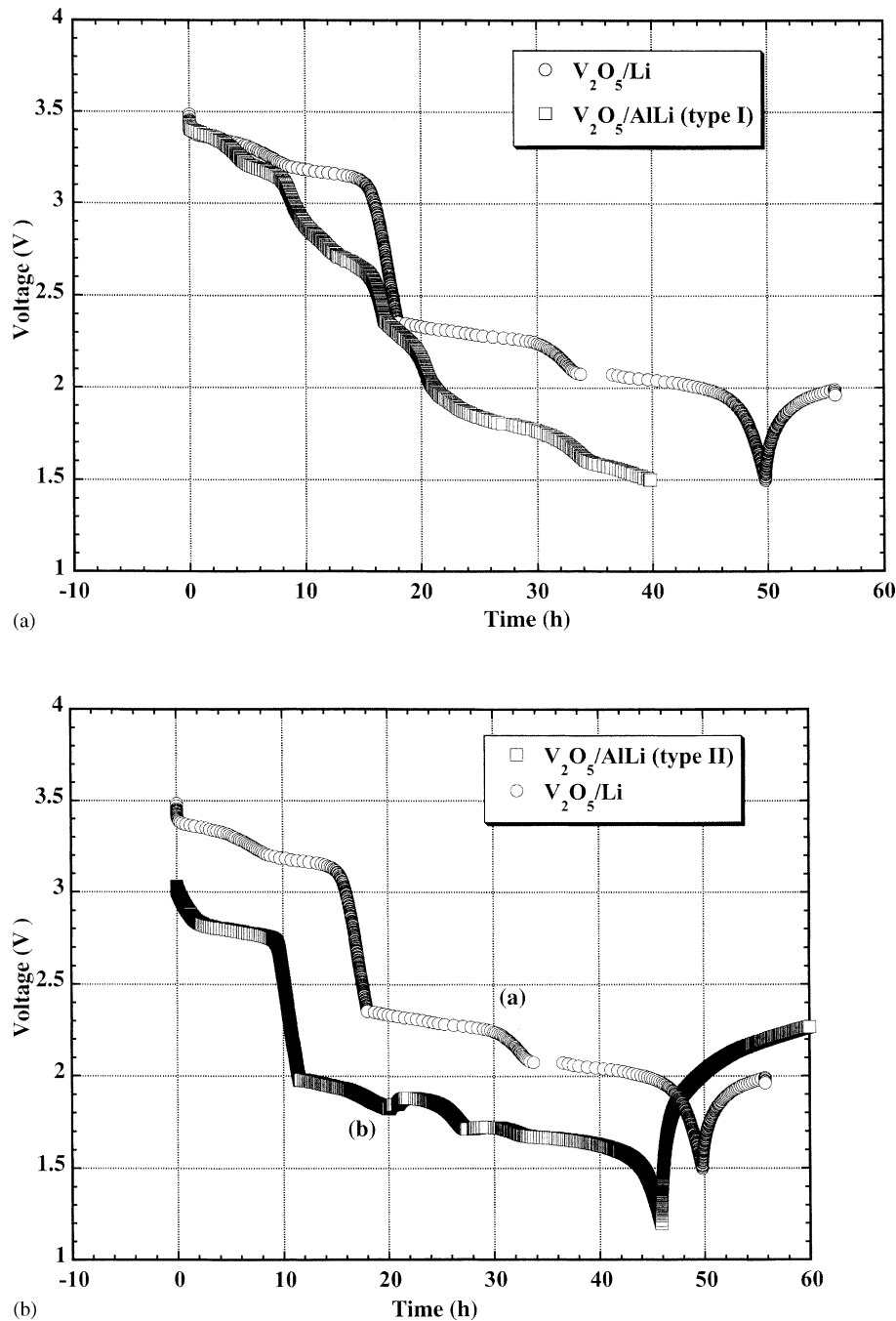


Fig. 7. Charge–discharge curves at 80 °C, (a) Type I cell (1st cycle); (b) Type II cell (1st cycle); (c) Type II cell (1st–7th cycles) and (d) Type III cell (1st cycle).

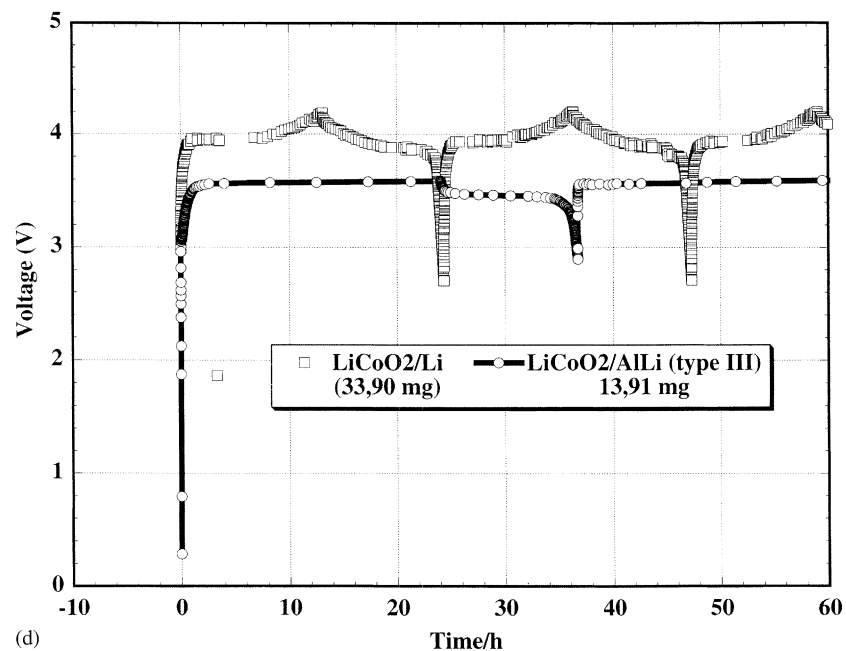
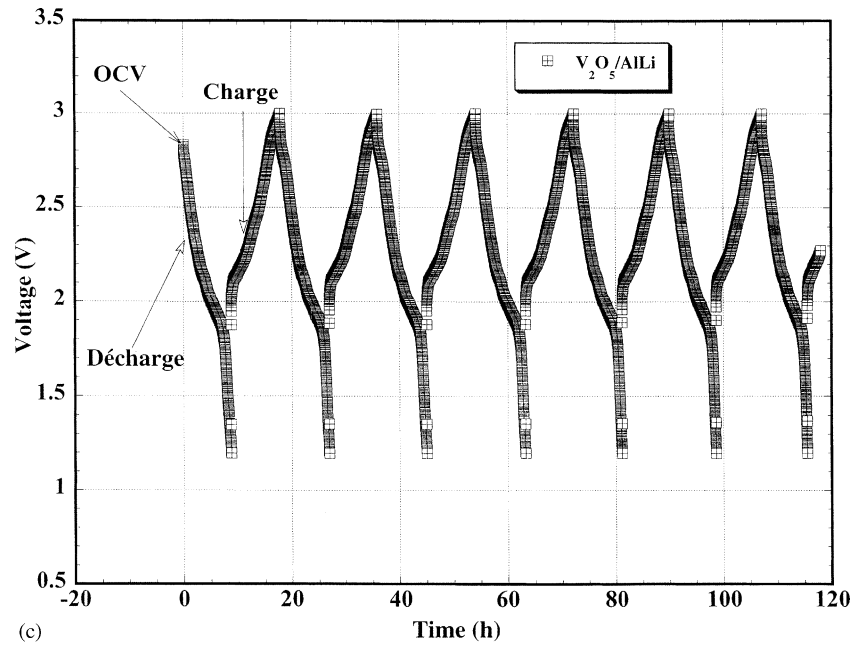


Fig. 7. (Continued).

different and the current collector is in contact with metallic lithium, as indicated in Fig. 3b. The initial discharge curve is also compared to that of an equivalent cell with a lithium anode (see Fig. 7b). It can be clearly observed that the performance is similar but that the average voltage is lower. This voltage decrease corresponds to the lower activity of lithium in the Li–Al alloy, i.e. about +435 mV versus Li^\ominus . The performance during cycling (Fig. 7c) of the cell using the alloy anode (see also Fig. 6) are stabilized and comparable with what is known from cells utilizing metallic Li. By way of reference, an identical cell utilizing an Al sheet

develops short circuits and loses some capacity even during the first few cycles.

The advantage of this device is that it permits assembly of a cell that can be activated, when needed. It is only when alloy formation is completed that the cell reaches full capacity, which makes cell assembly even safer. A test was conducted to demonstrate the safety of this cell in comparison with cell containing a metallic Li anode. The ARC measurement, shown in Fig. 8, were conducted with a full Type II cell weighing 0.5157 g, and a half-cell comprising a solid polymer electrolyte film and 22 μm thick Li.

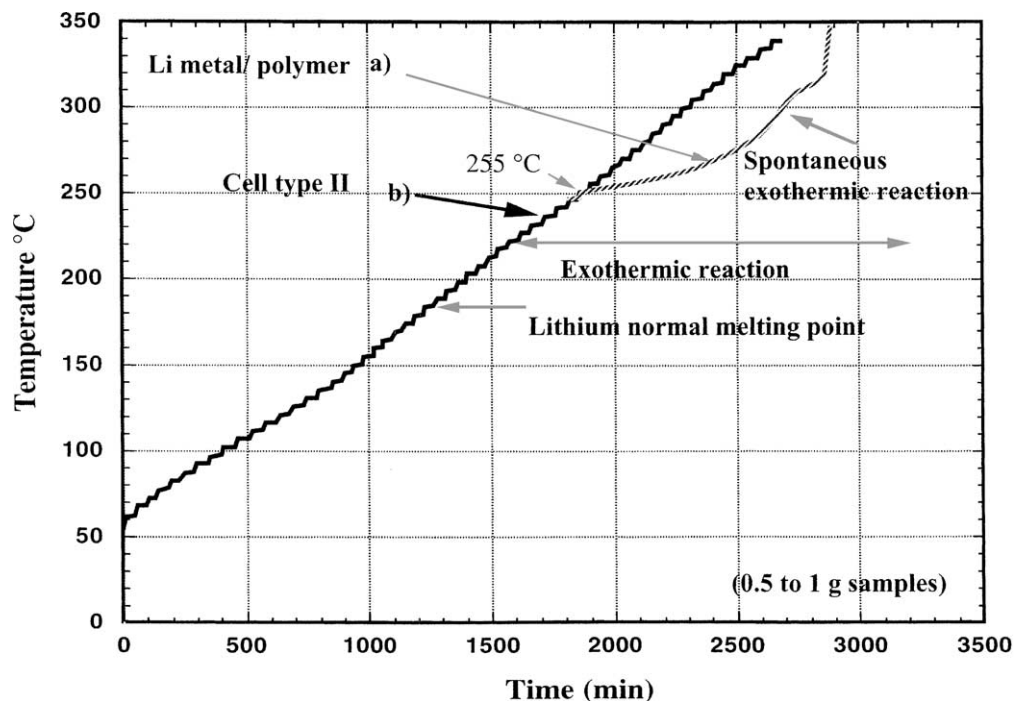


Fig. 8. Results obtained by ARC for a conventional cell and a cell using Al EXMET[®] as anode.

The temperature-rise curve (b) for the Type 2 cell indicates no self-heating occurred in the entire temperature range investigated. Under similar conditions, the sample without cathode and with metallic lithium (a) shows evidence for an exothermic reaction at about 255 °C, i.e. above the melting point of lithium (about 180 °C). A complete cell, i.e. containing a cathode, sometimes shows high exothermic heat resulting from a short circuit following the melting of lithium. This test is a good indication of the relative safety of the dense anode in a cells. In addition, an anode of Li alloy, which is a thin, dense film and non-fusible, will remain in a solid state at temperatures higher up to 300 °C.

3.2.3. Type III

In the Type III cell (see Fig. 3c), the Li source for the anode originates from the cathode (lithiated cobalt oxide) which is prepared in the discharged state. The anode and cathode capacity ratios were chosen to give the optimal performances in solid-state cells. The initial discharge curves are compared to that of an equivalent cell having a lithium anode (see Fig. 7d). The performances are similar but the average voltage is lower. This voltage decrease corresponds to the lower activity of Li in the Li–Al alloy, i.e. about +400 mV versus Li. The open circuit voltage (OCV) is 35 mV. The first-cycle coulombic efficiency is about 50%, similar to that obtained with solid-state Li-ion cells using natural graphite anodes: graphite (NG7)/SPE/LiCoO₂ [3], and 85% for Li/SPE/LiCoO₂. The irreversible capacity for Type III cells is higher than that of the equivalent cell with a Li anode. This is attributed to the formation of a passivation layer on the surface of the Al EXMET[®]. The

composite carbon may also contribute to the irreversible capacity; this effect will be discussed in a subsequent paper.

4. Concluding remarks

This work addressed the significance of local stress relaxation of Li alloy and dense Li sheets that were used as electrodes. Electrochemical cells with negative electrodes containing a sheet of expanded Al metal as a negative electrode were investigated. The advantage of expanded metal to accommodate lateral expansion to minimize changes in the plane of the electrode during alloy formation between Al and Li was demonstrated. Three types of cells were studied with charged or discharged cathode materials. The observation by in situ OM and in situ SEM helped develop a mechanism for local stress relaxation in the anode. The safety of the cells was also demonstrated by using the ARC technique. From an industrial point of view, the cell using aluminium film with holes (opening) coated with carbon or graphite as anode material appears to be a good choice for EV or HEV systems in terms of high energy density, safety and environmental benefits.

References

- [1] R.A. Huggins, NATO Sciences Series, vol. 85, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1999, p. 21.
- [2] M. Gilbert, K. Thomas, US patent, US 4,489,143 (1984).
- [3] K. Zaghib, M. Armand, M. Gauthier, J. Electrochem. Soc. 145 (1998) 3135.
- [4] R. Nesper, Prog. Solid State Chem. 20 (1990) 1.