

Advanced materials for negative electrodes in Li-polymer batteries

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Abstract

The active materials in commercial Li-ion batteries are usually graphitized carbons for the negative electrode and LiCoO₂ for the positive electrode. However, there is strong interest in alternative negative electrode materials with higher reversible capacity. The discussion in this paper is directed at analyzing the electrochemical performance of negative electrodes for Li-ion batteries. The physicochemical properties and the electrochemical performance of active materials in the negative electrodes are intimately connected, therefore both parameters are considered in selecting an alternative material to graphite. An analysis of this relationship is discussed in this paper.

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1. Introduction

The active materials in commercial Li-ion batteries are usually graphitized carbons for the negative electrode and LiCoO₂ for the positive electrode. The electrolyte usually contains LiPF₆ and solvents that consist of mixtures of cyclic and linear carbonates. The specific combination of Li salt and solvents in Li-ion batteries are critical for achieving acceptable performance and cycle life. For example, electrochemical intercalation of Li⁺ ions in graphitized carbon is difficult in LiClO₄/propylene carbonate (PC) because of rapid electrolyte decomposition and exfoliation of the crystallite structure. On the other hand, LiClO₄ in PC is an acceptable electrolyte for intercalation of Li⁺ ions in non-graphitized carbons (e.g., petroleum coke), but the electrochemical Li intercalation capacity is less, amounting to about 180 mA h/g C. Other amorphous carbons have been investigated, and some have electrochemical capacities that exceed 372 mA h/g C, which is the theoretical Li intercalation capacity of graphite.

Prior to the success of Li-ion technology, attempts to produce rechargeable lithium cells were frustrated by technical issues related to safety and the poor cycle life of metallic lithium electrodes. The morphological changes that occur during repetitive charge/discharge cycling of lithium eventually lead to cell failure. To overcome some of these problems,

alloys of lithium, such as Li–Al and Li–Si, were considered. Here again problems were encountered with mechanical stability of the alloys when the electrode was cycled. To date, lithium metal and lithium alloys have shown limited promise in practical rechargeable cells containing nonaqueous liquid electrolytes. However, various forms of Li alloys have attracted attention for use in Li-ion batteries. The announcement by Fuji Photo Film Co., Ltd. in Japan of a tin-based composite oxide (Sn_{1.0}B_{0.56}P_{0.4}Al_{0.42}O_{3.6}) for the negative electrode in Li-ion cells sparked widespread research to develop alternatives to carbon [1]. This finding shifted some of the attention from Li alloys to metal oxide-based materials as alternative negative electrodes for Li-ion cells.

The discussion in this paper is directed at analyzing the electrochemical performance of negative electrodes for Li-ion batteries based on experience in our laboratory. The physicochemical properties and the electrochemical performance of active materials in the negative electrodes are intimately connected, therefore both must be considered in selecting an alternative material to graphite in negative electrodes for Li-ion batteries. An analysis of this relationship is discussed in this paper.

2. Discussion

The two major types of negative electrodes for Li-ion batteries are carbon-based materials and metal oxide/nitride or metal–metal combinations. To date, only the carbon-based

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materials, mainly graphitic carbons, have found widespread use in commercial Li-ion batteries. However, the alternative materials have some attractive electrochemical properties that merit their consideration for negative electrodes in Li-ion batteries.

Three electrochemical parameters that play a significant role in the viability of negative electrode materials in Li-ion batteries are reversible capacity, irreversible capacity loss (ICL) and cycle life. Ideally, the negative electrode should have high reversible capacity, long cycle life and low ICL. Achieving this set of characteristics has been elusive, especially with alternative materials to graphite for negative electrodes in Li-ion batteries. Even if alternative materials possess high reversible capacity and long cycle life, they often have high ICL, which presents a problem in practical Li-ion cells.

Fauteux and Koksang [2] summarized the properties of various alternative negative electrode materials for rechargeable Li batteries. More recently, electrochemical studies of a wide range of alternative electrode materials have been reported, e.g., InSb [3], Sn–SnSb [4], Mg₂Si [5], Sn₂Fe–C [6], Li_xCu₆SnS₅ [7a], Cu₆SnS₅ [7b], LiNi–Sn [8], Sn–Mn–C [9], Li_{2.6}Co_{0.4}N [10], Si (33.3 mol%)/TiN composite [11], Li₄Ti₅O₁₂ [12], Li₂Ti₃O₇ [13], SnO₂ [14] and graphite–Fe₂₀Si₈₀ alloy composite [15]. The reversible capacity (mA h/g) of lithium metal is about 10 times that of the stage-1 lithiated graphite compound. On a volumetric basis, the reversible capacity (mA h/cm³) of lithium metal is only about 2.5 times greater. When a similar comparison is made between graphite and metal oxide/nitride or

metal–metal combinations, the differences in the reversible capacity (mA h/g) are smaller, but in some cases, the volumetric reversible capacities are larger.

2.1. Carbon-based negative electrodes

Fig. 1 shows the charge–discharge profile obtained with natural graphite of different average particle size in 1 M LiClO₄ in 1:1 (volume ratio) EC–DMC. With natural graphite, voltage plateaus associated with the staging phenomena observed with intercalation of Li⁺ ions between the layer planes are clearly evident. For the stage-1 compound ($x = 1$), LiC₆, the electrochemical capacity is equivalent to 372, and 186 mA h/g C for the stage-2 compound ($x = 0.5$), LiC₁₂. There is a strong relationship between the crystallographic properties of carbon and its reversible capacity [17]. A parabolic relationship with a minimum in x at a $d(002)$ spacing of 3.44 Å is evident. It may be coincidental, but by Maire and Mering [16] suggested that the degree of graphitization is equal to zero at $d(002) = 3.44$ Å. At $d(002) < 3.44$ Å, carbon has a graphitic structure, and Li⁺ ions are inserted between the layer planes. On the other hand, at $d(002) > 3.44$ Å, carbon has a turbostratic structure and the mechanism for insertion of Li⁺ ions involves other mechanisms [17].

In the case of graphite electrodes, the ICL is mitigated by use of low surface area graphites, as illustrated in Fig. 2. Because the reactions responsible for the ICL with graphite are surface reactions, there is a strong dependence on the surface area. A lower surface area is associated with larger

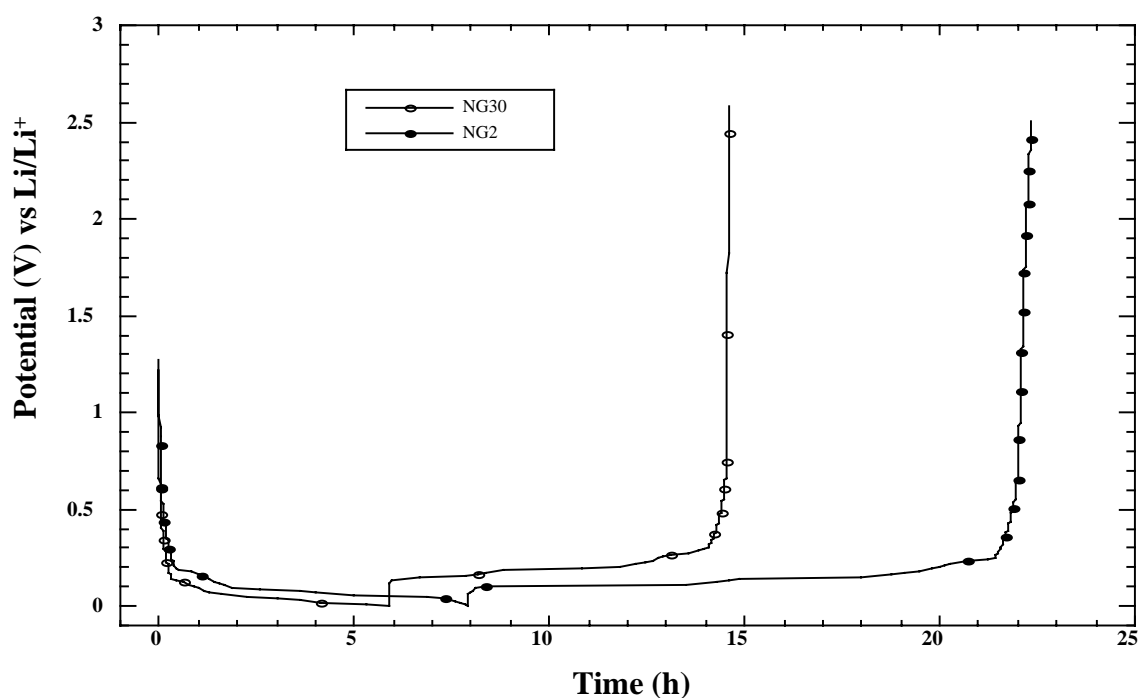


Fig. 1. Charge–discharge profiles for natural graphite of average particle 2 μm (NG2) and 30 μm (NG30). Discharge rate of 46.5 mA/g (C/8 rate) and a charge rate of 31 mA/g (C/12 rate).

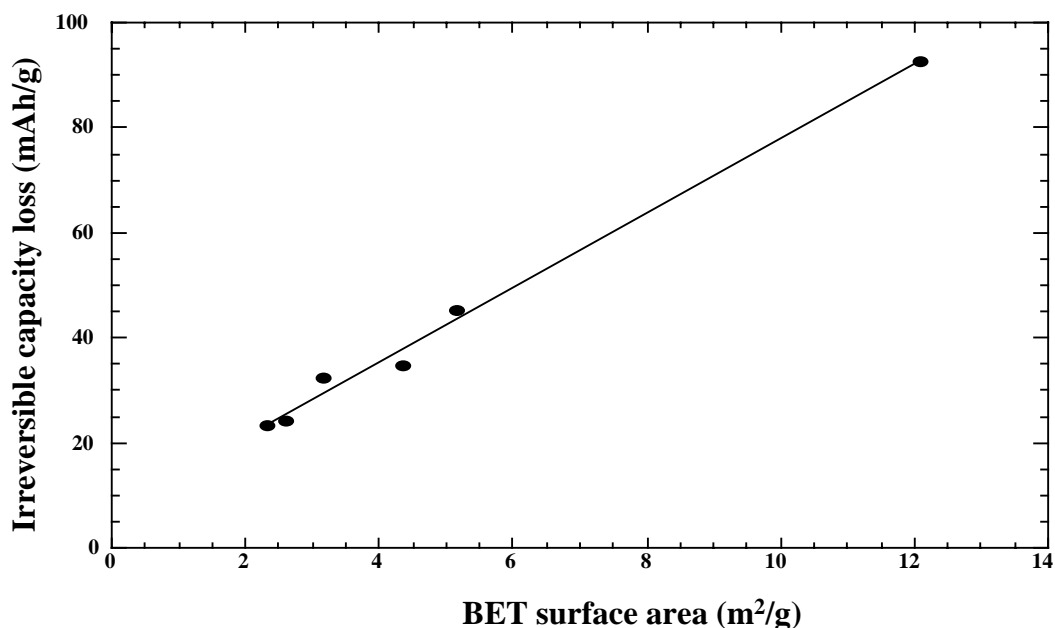
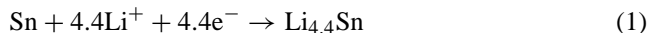


Fig. 2. Relationship between surface area and ICL of natural graphite electrodes for Li-ion cells.

particle size, consequently a compromise must be made to optimize the intercalation rate and reversible capacity while still maintaining a low ICL.

2.2. Alternative negative electrodes

Following the announcement by Fuji Photo Film Co., Ltd. of a tin-based composite oxide ($\text{Sn}_{1.0}\text{B}_{0.56}\text{P}_{0.4}\text{Al}_{0.42}\text{O}_{3.6}$) for the negative electrode in Li-ion cells [1], attention has been focused on Li alloys and lithiated metal oxides. Taking the example of Sn and one of its common oxides, SnO_2 , the electrochemical reactions that take place during charge can be illustrated by the following:



During charge, Li_2O is formed irreversibly, and the amount that is formed is indicative of the ICL. With SnO_2 , for example, ICL can be >40% or 850–1000 mA h/g [14,18–20]. Upon reversal of the current (discharge), the Li–Sn alloy reacts (de-alloy) reversibly while Li_2O is essentially inert. During the initial charge of the negative electrode, electrolyte decomposition takes place when the electrode potential is decreased to less than about 0.8 V. The extent of this reaction, along with the reactions involving the formation of Li_2O , is associated with the ICL. In addition, parasitic reactions of the alloy or metal oxide occur that contribute to the ICL. In the above example with Sn-containing compounds, SnO_2 forms Li_2O that remains essentially inert during cycling. The Li storage capacity of $\text{Li}_{4.4}\text{Sn}$ is equivalent to 790 mA h/g, which would provide a clear advance over that

of graphite (i.e., 372 mA h/g). However, its high ICL and low cycle life limits its applicability in practical Li-ion cells.

Changes in the volume of Li alloys are substantial compared to graphite during charge–discharge cycling, and this leads to mechanical degradation that contributes to limited cycle life. For comparison, graphite undergoes a volume change of 6%, in contrast to about 100% or greater with Li alloys of Al, Sn and Si [2]. A capacity fade of 3–6.9% per cycle were observed with SnO_2 and Sn, respectively by Kim et al. [21]. They also observed that homogeneous Sn oxide-based glasses ($\text{SnO}_2:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5 = 1:0.25:0.25$) with an amorphous structure (cluster size: 10–20 nm, grain size: ~5 nm) had capacity fade of 0.4% per cycle. The improved performance is attributed to the finer and more uniform distribution of the SnO_2 phase crystallized from the chemically derived precursors in the glass matrix compared to that of pure SnO_2 powder.

Several approaches have been identified to overcome the high ICL and poor cycle life of alternative anode materials, such as utilizing: (i) small particles; (ii) multiphase composition; (iii) materials that undergo phase separation and restoration.

The above-mentioned study by Kim et al. [21] illustrate the benefit of small particle size and multiphase composition to obtain improved cycling performance of alternative negative electrode materials. Yang et al. [4] earlier acknowledged the cycling improvements with small particles. The cycling stability increased with a decrease in the particle size of Sn–SnSb, and was higher for the multiphase Sn–SnSb than for the single-phase Sn of comparable particle size. The Sn–SnSb of particle size <300 nm yielded about 200 cycles.

Another approach to develop a viable alternative negative electrode is to utilize expanded metal (EXMET®). An

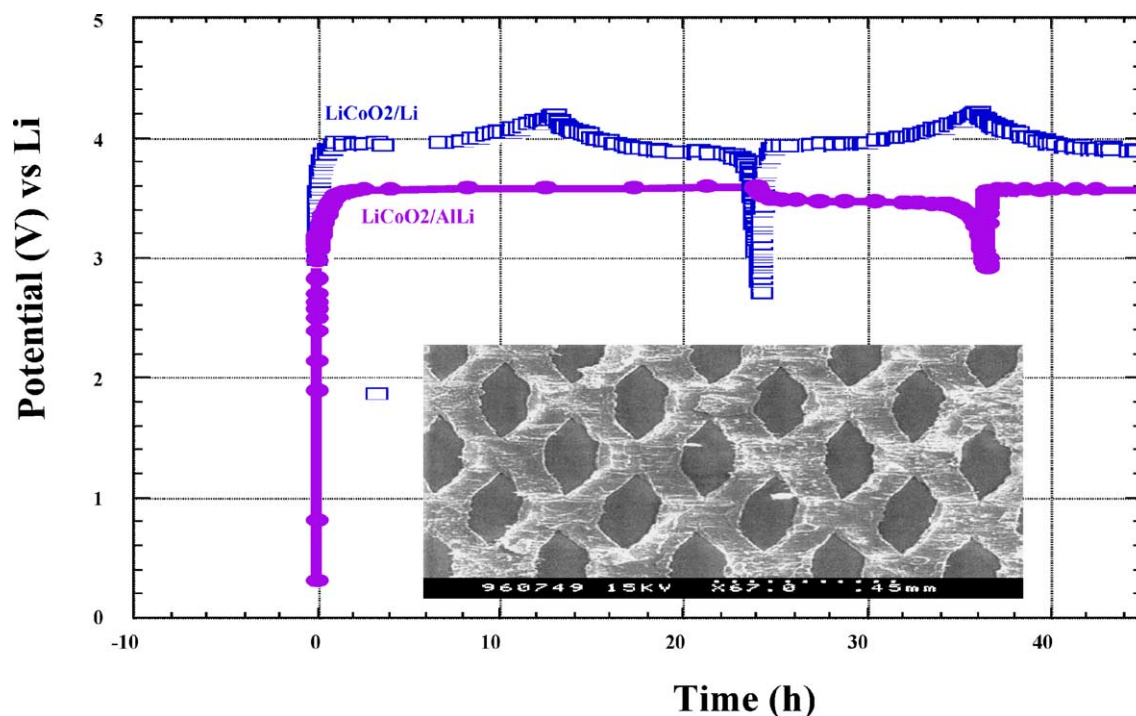
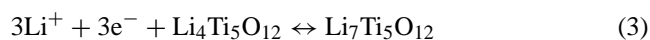


Fig. 3. Discharge-charge curves obtained with cells: Al EXMET[®]/LiCoO₂ cell with SPE and LiCoO₂/Li. Inset shows the SEM micrograph of Al EXMET[®].

Al EXMET[®], which is presented in the SEM micrograph in Fig. 3, was evaluated in a cell containing a solid polymer electrolyte (SPE) and LiCoO₂ positive electrode [22]. The Al EXMET[®] (25 μm thick after compressing, 50% void volume, and openings were ~145 μm across). The anode and cathode capacity ratios were chosen to give optimal performances in solid-state cells. 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. Observations by in situ microscopy showed that alloy formation in the mesh of the open structure produces a lateral expansion of about 10%, which is considerably less than the expected value of about 100% [22]. The initial charge and discharge voltage of Al EXMET[®] is lower than that of a LiCoO₂/Li cell because of the lower activity of Li in the alloy.

To avoid the issues connected with high ICL and mechanical degradation and low cycle life of negative electrodes, metal oxides like Li₄Ti₅O₁₂ were investigated [23].

Although Li₄Ti₅O₁₂ has low theoretical reversible capacity (175 mA h/g), no structural change (zero-strain insertion material) occurs during Li⁺ ion intercalation and de-intercalation reversibility (see Fig. 4), represented by:



The reversible capacity of Li₄Ti₅O₁₂ obtained by reacting TiO₂ + Li₂CO₃ and carbon at 850 °C was 161 mA h/g in LiClO₄ + EC/DMC. Because the mid-discharge voltage is close to 1.5 V, electrolyte decomposition is minimal and the ICL is low. In addition, safety is improved by operating at

high potential relative to lithium metal. The absence of passivation films on Li₄Ti₅O₁₂ because of the high operating potential gives rise to low internal resistance and consequently high power and long cycle life.

2.3. Comparison of graphite to alternative anode materials

Commercial Li-ion cells with graphite negative electrodes are manufactured in the discharged state (i.e., no Li in the carbon electrode), thus an excess amount of positive electrode material must be used to compensate for Li⁺ ions associated with the ICL, as well as the amount of Li for intercalation of graphite. When ICL increases, a greater fraction of the capacity of the positive electrode is irreversibly lost, and a lesser amount is available to contribute to the reversible capacity of the negative electrode. Consequently, the mass ratios of the negative and positive electrodes must be optimized, and this is critical with alternative negative electrodes. The important role that the ICL plays in Li-ion cells is illustrated by the following analysis.

Broussely et al. [25] discussed the impact of the insertion material properties on the characteristics of Li-ion cells from a manufacturer's point of view. Following up on the study by Broussely, we analyzed a number of physicochemical and electrochemical properties of negative electrode materials to ascertain the advantages and disadvantages of using alternative anode materials instead of graphite in Li-ion cells. This analysis relied heavily on the modeling studies of White and co-workers [26,27].

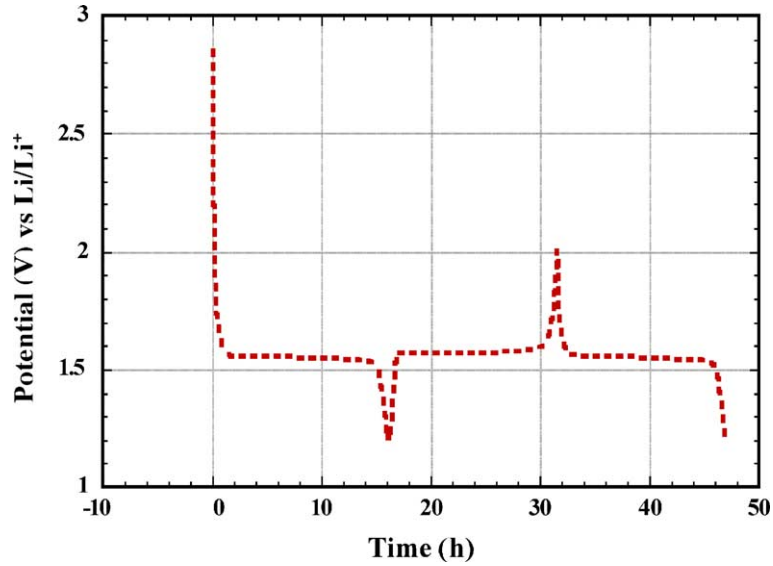


Fig. 4. Discharge-charge curves obtained with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in 1 M LiClO_4 in EC/DMC at C/24 rate.

An excess amount of positive electrode material must be used to compensate for the ICL in Li-ion batteries. The actual and theoretical mass ratios (γ) of the active materials in the positive (subscript +) and negative (subscript -) electrodes of Li-ion batteries are defined as [26,27]

$$\gamma_{\text{actual}} = \frac{m_+}{m_-} = \frac{\delta_+ \varepsilon_+ \rho_+}{\delta_- \varepsilon_- \rho_-} \quad (4)$$

and

$$\gamma_{\text{theoretical}} = \frac{\Delta x C_-}{\Delta y C_+} \quad (5)$$

respectively. The parameter m is the mass of active material in the composite electrode (g/cm^2), δ the electrode thickness (cm), ε the volume fraction of active material, ρ the density of active material (g/cm^3), C the theoretical coulombic capacity of insertion material based on discharged state (mA h/g), and x and y are the stoichiometric coefficients for the negative and positive electrodes, respectively. When the ICL and side reactions at the negative electrode are considered, this contribution (C_{irr}) yields

$$\gamma_{\text{actual}} = \frac{\Delta x C_- + C_{\text{irr}}}{\Delta y C_+} \quad (6)$$

The magnitude of C_{irr} represents the additional capacity needed during the initial formation cycles, and will impact the mass ratio of the active material in the negative and positive electrodes. The additional capacity can be defined in terms of a percent (i) of the reversible capacity, C_- . In other words

$$C_{\text{irr}} = i C_- \quad (7)$$

The relationship between the mass ratio (Eq. (4)) and electrochemical parameters (Eq. (6)) yields

$$\frac{\Delta x C_- + C_{\text{irr}}}{\Delta y C_+} = \frac{\delta_+ \varepsilon_+ \rho_+}{\delta_- \varepsilon_- \rho_-} \quad (8)$$

which leads to

$$\frac{\delta_+ \varepsilon_+ \rho_+}{\Delta y C_+} = (\delta_- \varepsilon_- \rho_-) (\Delta x C_- + C_{\text{irr}}) \quad (9)$$

Eq. (9) is useful to compare the properties of different negative electrodes in combination with the same positive electrode. Taking the electrode thickness of the negative electrode, for example, the following equation is derived from Eq. (9):

$$(\delta_-)_a = \frac{[(\delta_- \varepsilon_- \rho_-) (\Delta x C_- + C_{\text{irr}})]_g}{[(\varepsilon_- \rho_-) (\Delta x C_- + C_{\text{irr}})]_a} \quad (10)$$

where the subscripts a and g refer to the alternative anode and graphite, respectively. Eqs. (7) and (10) are used here to compare the relative thickness of a carbon (graphite) electrode to that of an alternative anode in Li-ion cells that contain the same type of positive electrode. To make this analysis, some characteristics of the negative electrodes must be assumed, and are based on values suggested by Brousely et al. [24]. The densities of carbon and the alternative anode are assumed to be 2.2 and 5 g/cm^3 , respectively. The corresponding volume fractions of these materials are 0.36 and 0.5, respectively. The thickness of the carbon electrode is set at 100 μm , and the alternative anode thickness is a variable that depends on the reversible capacity and ICL.

Assuming that ICL equals 15% for the carbon electrode, the results plotted in Fig. 5 are obtained for the relationship between the thickness of the alternative anode and its reversible capacity and ICL. The thickness of alternative anodes decreases as the reversible capacity increases and the ICL varies between 5 and 30%. This trend is attributed to the fact that the capacity of the positive electrode is fixed, and it limits the amount of Li^+ ions available for electrochemical reaction at the negative electrode. When the

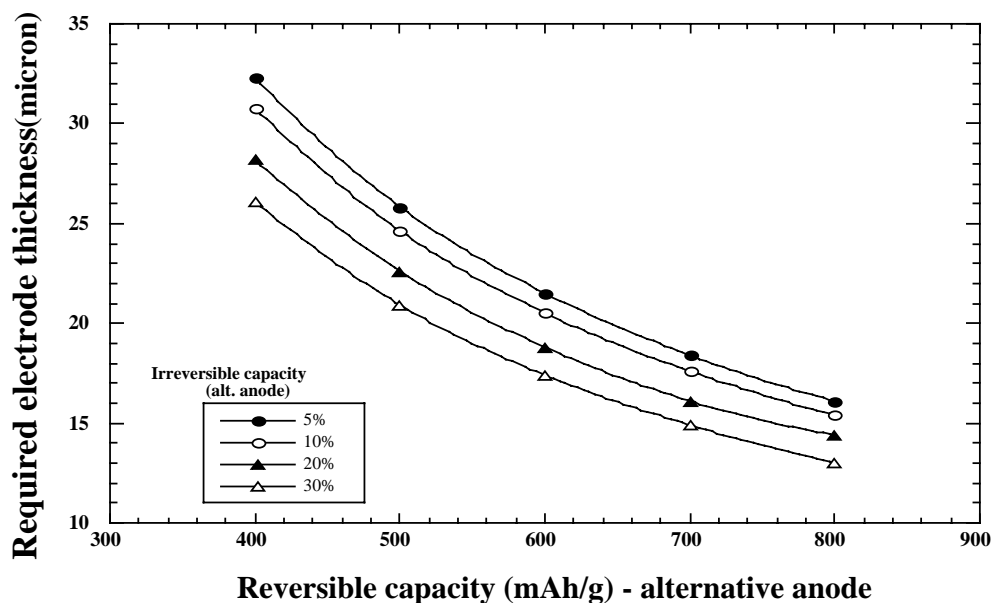


Fig. 5. Relationship between the thickness of an alternative negative electrode and its reversible capacity and ICL. The properties of the carbon electrode used in the analysis are assumed to be constant (see text).

above-mentioned assumptions are made, Eq. (10) can be simplified to

$$(\delta_-)_a = \frac{K}{[(\Delta x C_- + C_{\text{irr}})]_a} \quad (11)$$

where K is a constant that incorporates the properties of the graphite electrode and the volume fraction and density of the alternative anode ($\varepsilon_- \rho_-$). In this situation, the thickness of the alternative electrode is dependent on the reversible capacity and ICL. For a given reversible capacity of an alternative anode, its thickness decreases if ICL increases. Take for example an alternative anode with a reversible capacity of 500 mA h/g. Its thickness decreases from 26 μm with 5% ICL to 21 μm with 30% ICL. Therefore, when the ICL increases, a greater fraction of the capacity of the positive electrode is consumed in ICL. The consequence is that the alternative anode must be thinner because of the limited capacity of the positive electrode. Furthermore, the electrode thickness of the alternative anodes is much less than that of graphite, which is assumed to be 100 μm thick. These observations suggest that any gain in reversible capacity that is attained with alternative anodes must be balanced with the minimum electrode thickness that can be readily fabricated. A more sophisticated analysis and improved model would be helpful to determine the optimum combination of positive electrode and alternative anode for Li-ion batteries.

3. Concluding remarks

It still remains to be seen, if an alternative negative electrode will be developed in the near term to supplant carbons

in commercial Li-ion batteries. However, there is still a need to improve the performance and safety, as well as reduce the cost of Li-ion batteries. Successful development of alternative negative electrodes would be one step in that direction.

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