

Graphite vs. Lithium-Alloy Anodes in Lithium Ion Batteries

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Introduction

The active materials in the electrodes of commercial Li-ion batteries are usually graphitized carbons in the negative electrode and LiCoO₂ in the positive electrode. The electrolyte contains LiPF₆ and solvents that consist of mixtures of cyclic and linear carbonates. Electrochemical intercalation is difficult with graphitized carbon in LiClO₄/propylene carbonate (PC) because of rapid electrolyte decomposition and exfoliation of the crystallite structure. Successful intercalation of Li^e ions into graphite was made possible by using a mixed solvent electrolyte system such as LiPF₆ in ethylene carbonate (EC) + diethyl carbonate (DEC). On the other hand, LiClO₄ in PC is an

acceptable electrolyte for intercalation of Li⁺ ions in nongraphitized carbons such as petroleum coke, but the electrochemical Li capacity is less, amounting to about 180 mAh/g C. Other amorphous carbons have been investigated, and some have electrochemical capacities that exceed 372 mAh/g C, which is the capacity of graphite. For transportation applications, safety, cost and calendar life are key technical issues that must be resolved. One approach to understanding and resolving these issues is to utilize mathematical models that can guide experimentalists in their development efforts to identify improved electrode components. Lithium-alloy anode for rechargeable lithium batteries, in particularly phase equilibria and transport properties [1, 2] have been extensively studied long before carbonaceous materials. An obvious advantage of Li insertion into metallic matrices compared with Li-graphite intercalation compounds is the high packing density of Li that can achieve in Li alloys (see table1). In many case the packing density of Li-alloy is very close to than in metallic Li (e.g. Li₂₁, Si₅)

The discussion in this paper is directed at the electrochemical performance of negative electrodes for Li-ion batteries that could benefit from mathematical models. The physicochemical properties and the electrochemical performance of active materials in the negative electrodes are intimately connected, therefore both must be considered in a viable model. With this in mind, the significant physical properties of negative electrodes for Li-ion batteries are summarized, and the relationship of these properties to their electrochemical performance in no aqueous electrolytes, are discussed.

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. [3] 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 Brussels, 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. 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 (m) of the active materials in the positive (subscript +) and negative (subscript -) electrodes of Li-ion batteries

$$m_{\text{actual}} = m_+/m_- = (\rho_+ \rho_+ \rho_+)/(\rho_- \rho_- \rho_-) \quad \text{and}$$

$$m_{\text{theoretical}} = (\rho_+ x C_-)/(\rho_- y C_+)$$

The parameter m is the mass of active material in the composite electrode (g/cm²), ρ is the electrode thickness (cm), ρ is the volume fraction of active material, ρ is the density of active

material (g/cm³), C is the theoretical coulombic capacity of insertion material based on discharged state (mAh/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

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.

References

1. R. A. Huggins et al, J. Electrochem., Soc, 133 (1986) 457
2. J.O Bessenhard in W. Muller-Warmuth (eds.), Kluwer, Dordrecht, 1994, P457
3. M. Broussely, presented at "Lithium Battery Discussion: Electrode Materials," Arcachon, France, May 27- June 1, 2001

	Ah/g	Ah/cm ³	D : g/cm ³	Color
Li	3,82	2,02	0,53	
LiC₆	0,33	0,67	2	Or
Li₂₁Si₅	1,97	2,28	1,16	Metallic silver
Li₃As	0,84	2,04	2,43	Red-brown
LiAl	0,79	1,38	1,75	Gray -bleu
Li₂₁Sn₅	0,76	1,94	2,55	Metallic gray
Li₃Sb	0,56	1,79	3,17	Metallic gray
Li₂₂Pb₅	0,50	1,92	3,88	Metallic black

Table 1