Effect of Particle Morphology on Lithium Intercalation Rates in Natural Graphite:
3-Dimension versus 2-Dimension

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Introduction

Theoretical analyses of intercalation electrodes conducted by a number of researchers showed that the particle size, particle surface area, solid-state and liquid-phase diffusion rates of intercalant ions, electrode thickness and electrode porosity have a significant influence on the charge-discharge rates and utilization of intercalation electrodes. Verbrugge and Koch (1) analyzed the charge-transfer reaction and diffusion of intercalants in porous electrodes. They defined a parameter $\square$ to determine the relative importance of solid-state transport resistance to that of the liquid phase:

$$\square = [D_{salt}/D_I^o][r_s/L]^2$$

where D_{salt} is the salt diffusion coefficient, D_I^o is the intercalant diffusion coefficient at infinite dilution, r_s is the characteristic dimension of the particle, and L is the thickness of the porous electrode. When $\square$ is large, solution-phase diffusion resistance does not need to be considered. With typical values quoted by Verbrugge and Koch ($D_{salt} = 5.5 \times 10^{-6}$ cm^2/s, $D_I^o = 1 \times 10^{-10}$ cm^2/s, $r_s = 0.3$ µm, L = 20 µm), $\zeta = 12.375$, so only solid-state diffusion should be considered. Fuller et al. (2) also analyzed transport in solution and intercalation electrodes utilizing a dimensionless parameter S_S that is a ratio of the diffusion time in the electrode to the discharge time. They concluded that diffusion limitations may exist in carbon. The intent of the present paper is to extend these studies by providing a systematic analysis of a series of natural graphite flakes with different morphologies (i.e., 3-dimension and 2-dimension particles) but different average particle size.

Experimental

Six samples of prismatic flake natural graphite powders (2-dimension) with average basal plane dimension of 2, 7, 12, 20, 30 and 40 µm were obtained from a commercial source. The edge thickness of these samples ranged from 0.21 µm to 2.85 µm, as determined from scanning electron microscopy. The d_{002} spacing determined by x-ray diffraction analysis is 3.36 Å and is essentially the same for all of the samples. The basal length of the particles is taken to be the same dimension as the average particle size. The physical properties of these samples are summarized elsewhere (3). Four samples of sphere-like natural graphite powders (3-dimension) with average particle size of 12, 20, 30 and 40 µm were obtained by a mechanical process (Fig1). Two exfoliated graphite (2-dimension) from Grafite Brazil (10 and 20 µm) were also evaluated.

Results and Discussion

Fig. 2 shows representative data for the capacity versus current density for 20-µm prismatic and sphere-like morphologies. At low discharge rates. the capacities obtained with the two morphologies are similar. At higher discharge rates, the capacity of the 3-dimension structure remains relatively high. However, the capacity of the prismatic structure decreases sharply with current density because a lower amount of Li$^+$-ions was intercalated in the graphite structure. At higher discharge rates, the potential of the samples reached 0 V much sooner than the time indicated by the C-rate. Because of the slow transport rate of Li$^+$ ions in the graphene layer planes, the time is too short for the ions to completely intercalate the larger graphite particles to the theoretical limit. Slow solid-state diffusion of Li$^+$ ions produces concentration polarization in graphite that drives the potential towards 0 V, and this cut-off potential is reached before intercalation is complete. However, for the particles with a 3-dimensional morphology, the edge fraction f_e (3) is higher than f_e for the 2-dimensional morphology which gives a rapid solid-state diffusion of Li$^+$ ions. These results suggest that the 3-dimensional graphite morphology is more suitable for Li-ion batteries requiring high-rate charge/discharge such as in HEV and EVs.

Reference

1.   M. Verbrugge et al, J. Electrochem. Soc., **146**, 833 (1999).
2.   T. Fuller et al, J. Electrochem. Soc., **141**, 1 (1994).
3. K. Zaghib, G.Nadeau and K. Kinoshita, J. Electrochem. Soc., **147**, 2110 (2000).

Acknowledgment

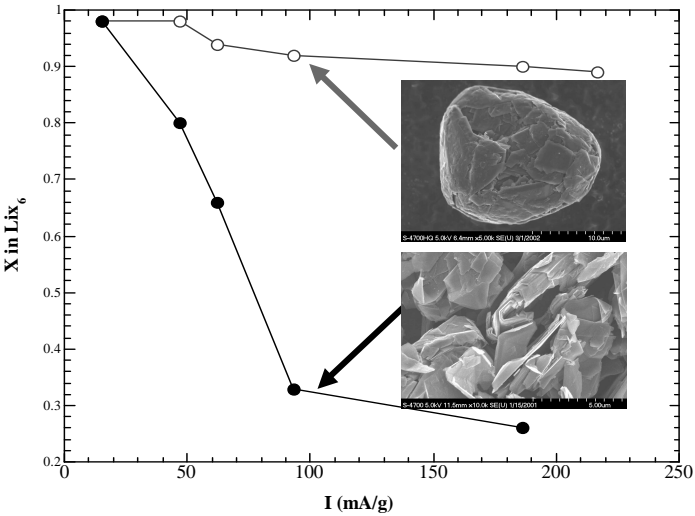Fig. 2. Capacity versus current density for graphite with 2- and 3-dimensional morphologies
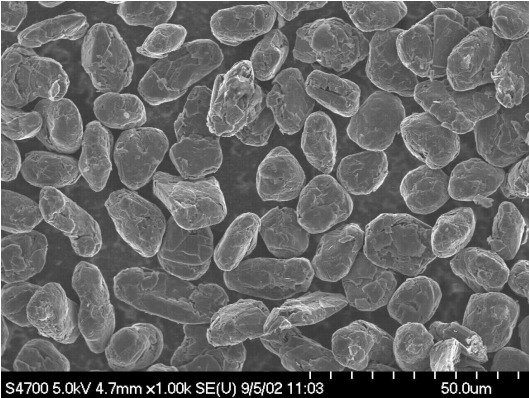
Fig. 1. SEM micrograph of 3-dimensional natural graphite
With average particle size of 12 µm.