Effect of Particle Size on Lithium Intercalation Rates in Natural Graphite for Li-ion Batteries

K. Zaghib, G. Nadeau, A. Guerfi, and
K. Kinoshita*

Institut de Recherche d'Hydro-Québec, 1800 boul,
Lionel-Boulet, Varennes, Québec, Canada, J3X 1S1
*Environmental Energy Technologies Division,
Lawrence Berkeley National Laboratory, Berkeley,
CA 94720, USA

Introduction

Theoretical analyses of intercalation electrodes have been conducted by a number of researchers. These studies show that the particle size, particle surface area, solid-state and liquid-phase diffusion rates of intercalant ions, electrode thickness and electrode porosity can have a significant influence on the charge-discharge rates and utilization of intercalation electrodes. For example, Verbrugge and Koch analyzed the charge-transfer reaction and diffusion of intercalants in porous electrodes. Their results are useful for analyzing the charge-discharge behavior of graphite electrodes for Li-ion batteries. They defined a parameter ζ that is a reflection of the relative importance of solid-state transport resistance to that of the liquid phase:

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

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 ζ 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), $\zeta = 12.375$, which suggests that only solid-state diffusion should be considered. Fuller et al. also analyzed transport in solution and intercalation electrodes and defined 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 in their analysis.

Studies of the charge-discharge rate capabilities of carbon particles considered for Li-ion batteries were reported in several publications... The intent of the present paper is to extend these studies by providing a systematic analysis of a series of natural graphite flakes with similar morphology but different average particle size

Experimental

Six samples of flake natural graphite powders 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 measurements using scanning electron microscopy. The d_{002} spacing, which was 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 were summarized elsewhere (1).

Results

Fig. 1 shows representative charge-discharge profiles for NG2 and NG30 at a discharge rate of 46.5 mA/g (C/8 rate) and a charge rate of 31 mA/g (C/12 rate). The profiles show that NG2 discharged for 8 h before the potential reached 0 V, and the corresponding time for NG30 was 6 h. The time for charge of NG2 was equal to the rate (C/12), whereas the time for NG30 was less (8 h) because the Li$^+$-ion content in the intercalated graphite was less. At the 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.

References

1. K. Zaghib, G. Nadeau and K. Kinoshita, J. Electrochem. Soc., **147**, 2110 (2000).

Fig. 1