Origins of composition delay in the stage 2 ? stage 1 phase transformation

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Introduction:
Lithiated graphite phases Li_xC_6 undergo a series of stage transformations as the Li composition varies from 0 to 1. Stage transitions translate into voltage plateaus in the OCV(x) curve of a Li/Li_xC_6 cells. It is commonly accepted that the voltage plateau in the x=0.5-1 composition range is associated with the stage 2 ($Li_{0.5}C_6$) to stage 1 (LiC_6) reversible transition. In this paper we give XRD evidences of composition delay in that transition. Starting from pure stage 2 compound, we show that stage 1 is observed at Li composition around 0.7-0.75, which is higher than theoretical x=0.5. A delay is also observed during the stage 2 formation from stage 1. These observations question the simple mechanism of phase transition between the two Li-rich stages $Li_{0.5}C_6$ and LiC_6.

In-situ XRD:
The experimental in-situ XRD cells consisted of CR 2016 coins cells having a window on the graphite side can. Graphite composite electrodes were made by casting a mixture of PVDF, carbon and 75wt% natural graphite on a Teflon mold. Cells contain lithium counter electrode, 1 molar $LiPF_6$ in EC:DMC (1:1) electrolyte and a Celgard separator. The cells were cycled using various galvanostatic slow rates varying from C/10 to C/60 on an Arbin cycler. The XRD scans were collected with an Inel CPS 120 using the Cobalt K_a radiation.
Figure 1 shows the evolution of the XRD charts for lithium concentrations ranging from 0 to 1. During Li intercalation (top figure) the strongest (001) peak of stage 1 appears only at x>0.7. Similarly during de-intercalation the 002 peak from residual stage 2 started to increase only below x~0.4. The OCV(x) curves however showed a plateau starting at x=0.5 and ending at x=1.

Structure models:
To observed composition delay in the stage 2 ? stage 1 transition suggest a Li-richer stage 2 compound may form. It is known that superdense phases exist in the stage 1 Li-graphite compounds. In theses phase the Li-Li distance in lower than in the classical hexal structure. Since graphite has a small concentration of defects, we believe a superdense stage 2 compound may form in the x=0.5-0.75 compositions range. During the stage 1 ? stage 2 transition, the mechanism may involve Li removal from all layers so as a "dilute" stage 1 compound may form before stage 2.
Preliminary first principle calculations using the Vienna Ab initio Simulation Package Code (VASP) and the Local Density Approximation formalism show that in $Li_{0.66}C_6$ a "pseudo stage 1" structure with two types of Li layers: a normal (hexal) layer and a dilute layer is thermodynamically more favorable than the stage 2 + stage 1 mixture. A model of such a structure is shown in figure 2.

Acknowledgments
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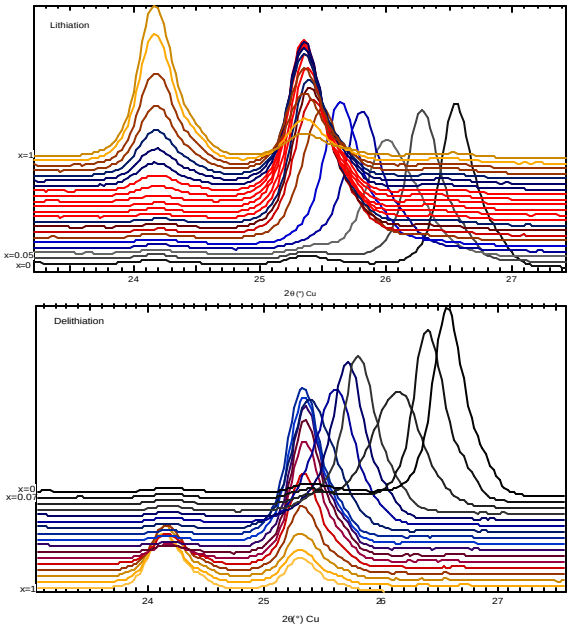

Figure 1: In situ XRD charts evolution during Li intercalation (top) and de-intercalation (bottom) into natural graphite

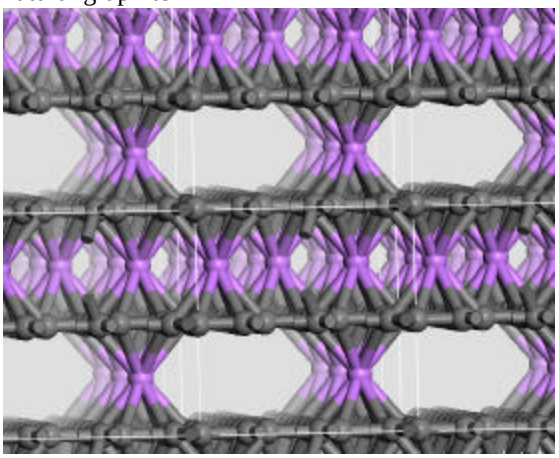

Figure 2: Stacking model in the $Li_{0.66}C_6$ "pseudo stage 1" compound showing two different Li density layers.