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The relative effects of composition and diffusion in the Si-M (M = Mn, Fe, Cr, Ni) system.

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Negative material systems containing amorphous Si offer the potential of high capacity and excellent capacity retention[1]. Recent investigations of the amorphous Si-Al-Mn system demonstrate that small changes in transition metal content have a dramatic effect on capacity[2]. The effect of transition metal content on the electrochemistry of Si-Al-M (where M is a transition metal such as Fe, Cr, Mn or Ni) systems is not well understood. Our aim is to understand both the Si-M and Al-M systems separately and then apply the results to Si-Al-M systems.

Previous work on various transition metal silicides suggests that any capacity between Si_2M (where M is a transition metal such as Cr, Fe, Mn, Ni) and Si is the result of Si not associated with transition metal atoms[3,4]. Weydanz *et al.* noted that electrochemical insertion of Li into $CrSi_2$ was very slow at room temperature[5]. We are extending these investigations by electrochemically cycling distinct compositions in broad composition ranges of Si-M_1-M_2 (M_1 and M_2 = two of Cr, Fe, Mn, Ni, and others). at various temperatures (room temperature, 55 and 70 ^{0}C), and cycling conditions. PITT measurements will also be used to determine the relative rates of Li diffusion in the various test materials. The observed capacities will be compared to equilibrium and non-equilibrium phase diagrams.

Thin films of Si-M_1-M_2 were sputter-deposited on to a variety of substrates, including the combinatorial electrochemical cell plate shown in Figure 1, using the technique described in [6]. The combinatorial electrochemical cell described in [7] was modified for use in a laboratory oven. Details of the modified cell are shown in Figure 1.

Figure 2 shows differential capacity vs. voltage plots for $Cr_{0.15}Ni_{0.20}Si_{0.65}$ cycled at room temperature, 55 and 70 ^{0}C. The capacity increases from approximately 230 to 430 mA h/g. Capacity increases with increasing temperature were smaller for materials with higher Si contents.

Figure 3 shows the 2nd discharge capacity as a function of composition from a Cr-Ni-Si experiment. It is interesting to note that contour lines of constant composition are approximately parallel to lines of constant Si content. Figure 4 shows discharge capacity as a function of transition metal content for Si-M (M=Cr, Fe, Mn, Si). Based on Figures 3 and 4 it appears that capacity depends only on the transition metal content, not on the specific transition metal used. Additional plots of capacity as a function of composition, and non-equilibrium phase diagrams for various Si-M_1-M_2 systems, will be presented.

References
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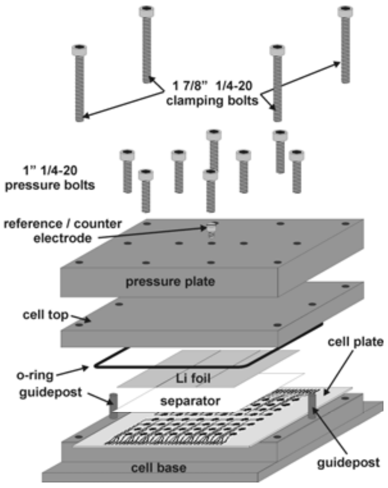

Figure 1. A pressure plate was added to the combinatorial electrochemical cell described in [7].

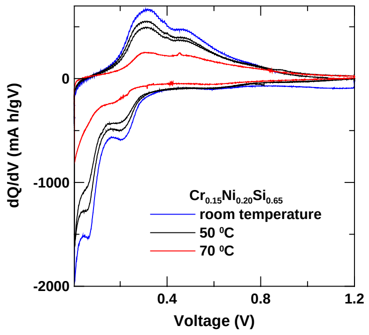

Figure 2. The shape of the differential capacity vs. voltage plot for $Cr_{0.15}Ni_{0.2}Si_{0.65}$ changes with cycling temperature. The capacity increases from 230 to 430 mA h/g.

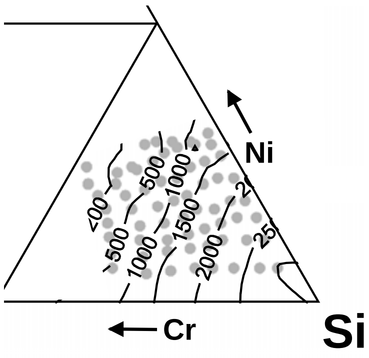

Figure 3. 2nd discharge capacity (mA h/g) vs. composition for Cr-Ni-Si. Grey dots indicate the compositions tested.

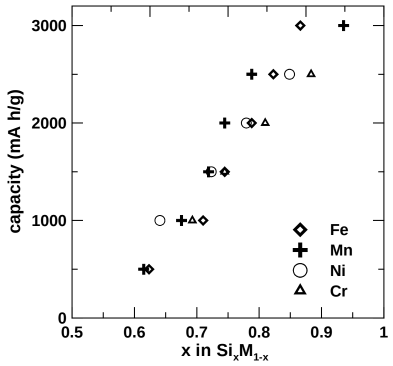

Figure 4. Capacity (mA h/g) vs. composition for Si_xM_{1-x} (M = Cr, Fe, Mn, Ni) at room temperature.