New High Rate Cathodes for Lithium Intercalation - W. Smyrl, G. Deluga, E. Frabretti (University of Minnesota\\ Corrosion Research Center/Dept of Chem Eng & Mat Sci), and M. Giorgetti (Dept of Physical and Inorganic Chemistry\\ University of Bologna)

There is current interest in the fundamental intercalation science of high rate intercalation into nanostructured porous hosts. Sol-gel techniques and related synthesis methods have led to the discovery of new materials with outstanding intercalation capacities and highly energetic thermodynamic properties. Aerogels and similar nanostructured porous hosts are among these new materials that promise one the opportunity to enhance the rates of intercalation without compromising their excellent thermodynamic characteristics. The present discussion will describe the kinetics and mechanisms of intercalation in porous and compact forms of the materials. We will explore interfacial charge transfer rates, and mobile and immobile sites for intercalation.

The intercalation of Li^+ ions into a thin, compact film of the host material is a coupled transport process with three different time constants. When viewed as a cyclic process, insertion and release at high frequencies are confined to the electrolyte/electrode interface as a charge transfer reaction and there is no change in concentration in the bulk of the host material. At lower frequencies, diffusion processes within the solid host dominate the behavior. At still lower frequencies in thin films of the host, concentration gradients do not develop in the bulk of the host, even though the total concentration of the guest changes during the process. In the latter region of behavior, one utilizes the entire mass (volume) of the host, but in the other higher frequency regions a smaller fraction of the host capacity is utilized as the rate of insertion is increased. The objective of studies on intercalation materials is to identify the limiting processes involved in insertion, and then to modify the structure so as to increase the insertion rate of guest cation species. Of particular interest is the enhancement of the charge transfer process (at high frequencies - region one above), an interfacial process. If we are able to eliminate solid state diffusion as a dominant process, interfacial charge transfer assumes a more crucial role in the intercalation process. The charge transfer process is not well characterized for many systems because in conventional work diffusion in the solid state dominates the insertion properties. Future research should explore ways to modify the charge transfer rate by modifying the nanostructure of the interface. A consequence of this will be to increase the useful utilization of the intercalation capacity of the host.

We have synthesized aerogels of V_2O_5 as high-rate, nanostructured hosts. The objective is to demonstrate that such materials eliminate solid-state diffusion as a fundamental limitation to the insertion/release process. It was expected that by preserving the bicontinuous network that is characteristic of the hydrogel precursor state one could obtain a porous material with very thin solid walls and thus very small solid state diffusion times (i.e. L^2/D, where L is half the solid wall thickness and D is the diffusion coefficient of the guest ion). The strategy has been successful, and intercalation impedance measurements have shown that solid-state diffusion at intermediate frequencies is eliminated. The typical solid wall thickness was 20 nm and the diffusion coefficient of Li^+ ions was about $10^{-11}cm^2/sec$. We have also used self-assembly in our studies of V_2O_5 nanoribbons that were grown on a conducting substrate. The nanofibers were about 10 nm thick and were 100 to 1000 nm long. Impedance showed that solid-state diffusion limitations were absent.

Pillaring of the layered structure of V_2O_5 by organic solvent species was discovered in our studies of intercalation of polyvalent cations into the host. The pillaring changes the interlayer spacing from 0.88 nm for nanoribbons of V_2O_5 0.5 H_2O to about 1 nm, depending on the species, and it is stable for many cycles of insertion and release. The significant finding for these materials was that polyvalent guests could be inserted to the same high intercalation capacity as for Li^+ ions. That is, 4 equivalents of Li^+ per mole of V_2O_5 was found to be the reversible capacity for lithium, 4 equivalents of Mg^{+2}, 3.33 equivalents of Al^{+3}, and 2.8 equivalents of Zn^{+2}. Of obvious interest is the question of whether there are both immobile and mobile sites in the intercalation host, and how one populates each. The discussion will include recent studies that focus on this question.

Modeling of the dynamics of insertion and how it is coupled with transport of the guest species is obviously quite important and we will discuss the mathematical approach for high rate materials in particular.