

Intercalation of Polyvalent Cations into V_2O_5 Aerogels

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Introduction

Sol-gel techniques for preparation of ceramics and structural oxides have become popular recently because of the great flexibility of synthesis and the varieties of structure that may be produced. In addition, the techniques may be used for the preparation of a large number of metal oxides of electrochemical interest. The preparation of intercalation hosts has been in the form of small particles of nanometer size, in the form of porous aerogels with surface areas of hundreds of square meters per gram and in the form of spin-coated and dip-coated compact films. The materials are often amorphous or nanocrystalline at low temperatures and may be crystallized by simple heat treatment at elevated temperatures. The procedures are readily adapted to large-scale manufacturing processes as well.

Aerogels are made by removal of liquid under supercritical conditions whereby the solid network that characterizes the gel state is preserved. In contrast, if the liquid is removed by normal air- or vacuum-drying below the critical point of the liquid, the characteristic three-dimensional network of the gel is collapsed and compact materials are obtained. The latter materials, called xerogels, are compact and have small surface areas, while the former, aerogels, may be obtained with high porosities and high surface areas. The high surface area of aerogels has been exploited for catalytic and electrochemical capacitor properties,¹ and the high porosity provides superior thermal insulation properties of some oxides.²

Aerogel intercalation materials are attractive hosts not only because of the high surface area but also because of the small diffusion distances in the solid that must be penetrated by the guest species. The small diffusion distance will support intercalation and release rates (of Li^+ ions for example) that are significantly enhanced over comparable xerogels. Our previous papers were the first to study intercalation aerogels^{3,4} in which it was shown that the Li^+ intercalation into V_2O_5 (ARG) occurred reversibly, at high capacity and

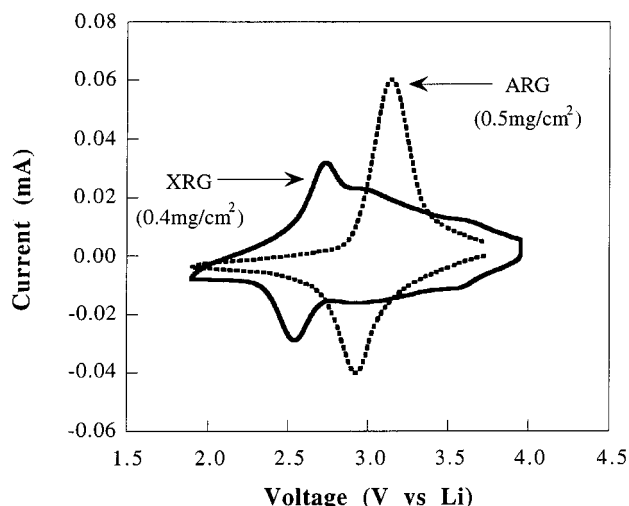


Figure 1. Current–voltage curves for insertion (cathodic) and release (anodic) of Li^+ ions in V_2O_5 (ARG) (solid curve) and V_2O_5 (XRG) (dotted curve), respectively. Electrolyte: 1 M $LiClO_4$ /propylene carbonate; T : 25 °C; sweep rate: 0.1 mV/s.

at high rates.⁵ Other work on V_2O_5 (ARG) has subsequently appeared,^{6–8} but the intercalation capacity was considerably smaller.^{6,7} As an example of the electrochemical behavior of V_2O_5 aerogel (ARG), Figure 1 is a current–voltage curve of a thin film. The reversible insertion and release of up to 4 Li^+ ions/mol of V_2O_5 has been demonstrated in this material.^{3,4}

In the present study, the intercalation properties of V_2O_5 (ARG) have been extended, and it will be shown below that the capacity for insertion of polyvalent cations is very comparable to that of Li^+ ions. These are the first reports of polyvalent cation insertion into any aerogel host. It will be shown here that 4 equiv of Mg^{2+} may be inserted per mole of V_2O_5 , identical to that of Li^+ .^{3,4} Further, the intercalations of Al^{3+} and Zn^{2+} are only slightly smaller, i.e., 3.33 and 2.5 equiv, respectively. We have used the chemical insertion method for the polyvalent cations, analogous to that previously used for Li^+ insertion into many host materials.^{9,10} Although V_2O_5 xerogel (XRG) has been demonstrated previously^{11,12} to be a versatile host for more than 20 different cations (including polyvalent cations), the level of intercalation was an order of magnitude smaller (i.e., 0.33 equiv/mol of V_2O_5) than we show here. Heat treatment of the metal-intercalated xerogels (MIX) have been carried out to form the respective “bronzes”, and these have been studied as Li^+ hosts.¹² The MIX mate-

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rials have also been studied as ionic conductors and dielectrics.¹² It was also observed previously that Mg^{2+} may be inserted into partially hydrated V_2O_5 xerogels,^{13–16} but insertion failed in dry organic solvent systems.¹³ Some limited insertion was observed in low-temperature molten salts¹⁴ and partially hydrated V_2O_5 bronzes.¹⁶

Experimental Section

Vanadium pentoxide hydrogels were synthesized by ion-exchange processing of sodium metavanadate (Fluka).¹¹ Aerogels were obtained by exchanging the water with acetone (EM Science, high-purity grade) and liquid CO_2 (Airgas, high-purity grade) and then carrying out supercritical drying with liquid CO_2 (1200 psi and 32 °C). The aerogel processing used a Samdri 780A supercritical drying apparatus (Tousimis Research Corp.). Aerogel powders were obtained by processing the liquid gel with no support. Typical chemical analysis (Galbraith Laboratories) showed that the aerogel contained about 0.4 mol of H_2O/mol of V_2O_5 . There was also 3.9% carbon that represents retained solvent (acetone) from the organogel intermediate. X-ray diffraction of the aerogel shows an interlayer spacing of 1.25 nm that may be attributed to the retained acetone, as compared to 0.88 nm which is characteristic of $V_2O_5 \cdot 0.5H_2O$ xerogel.¹¹

Chemical intercalation of the aerogel was carried out at room temperature by reaction with dibutylmagnesium (Aldrich), trimethylaluminum (Aldrich), and dimethylzinc (Aldrich), all in heptane. The intercalating reagent was titrated by reaction with a standard HCl solution. A known quantity of ARG powder was placed in a reaction vessel filled with an inert gas, and an excess amount of dibutylmagnesium, trimethylaluminum, or dimethylzinc, respectively, was introduced into the vessel by injection using an airtight syringe. The reaction was allowed to proceed under constant stirring for 1 week, and then the products were analyzed. The liquid from the reaction vessel was extracted, and heptane was injected several times to rinse out unreacted organometallic from the reaction vessel. The extracted solution was reacted with 2-propanol, and the product was titrated with standard HCl using phenolphthalein as an indicator. The difference between injected and unreacted organometallic corresponds to the amount of the respective metal cation intercalated into the sample. The powdered product was washed with excess heptane and submitted for elemental atomic absorption analysis (Galbraith Laboratories; also at the Geochemistry Laboratory, University of Minnesota). Portions of the powders were used in the equilibrium potential measurements and in the cyclic voltammetry experiments. This procedure is analogous to chemical lithiation as described by Murphy et al.⁹ and by Whittingham et al.¹⁰ There was excellent agreement between the titration results and elemental analysis results.

Open-circuit potential (OCP) measurements were performed on the chemically intercalated samples by pressing the dried powders of known metal cation content against a platinum mesh. The samples were then immersed in one compartment of the cell which had been filled with 0.1 M magnesium triflate ($Mg(CF_3SO_3)_2$, 3 M), 0.1 M Al triflate ($Al(CF_3SO_3)_3$, 3 M), or 0.1 M zinc triflate ($Zn(CF_3SO_3)_2$, 3 M), respectively, in dry propylene carbonate (Fluka). The other compartment had a solution of 1 M $LiClO_4$ (Fluka) in dry propylene carbonate into which a Li foil electrode was immersed. The two compartments were joined with a fritted glass disk to permit the formation of a liquid junction between the two electrolytes. We estimate that the liquid junction potential is, perhaps, a few tens of millivolts. The equilibrium potentials between the

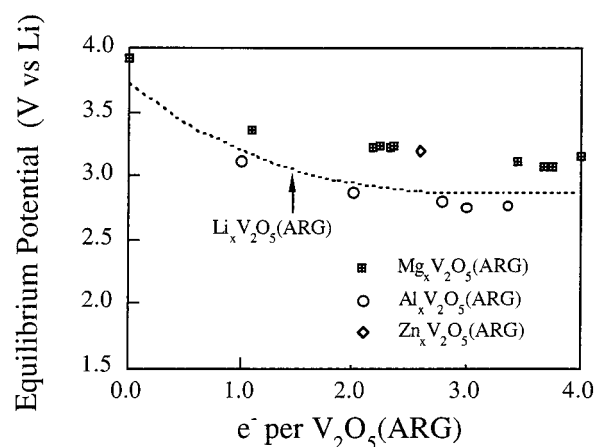


Figure 2. Thermodynamic equilibrium potential vs composition for intercalation of Mg^{2+} , Al^{3+} , and Zn^{2+} into V_2O_5 (ARG) and compared to the analogous lithium system.

two electrodes were measured with the electrometer of an EG&G/PAR 173 potentiostat.

Cyclic voltammetry experiments were performed on the chemically intercalated samples. Since there has been limited study of polyvalent metal systems in nonaqueous solutions, there are no well-defined reference electrodes for use for cyclic voltammetry. As a result, preliminary experiments were run with a two-electrode configuration. The dried powders of known metal cation content were pressed between two porous carbon foils (current collector) and used as counter electrodes. Virgin V_2O_5 aerogel electrodes, made in the same way, were used as working electrodes. Solutions of the corresponding cation-triflate salts in dry propylene carbonate were used as electrolyte. Since the solubility of the Mg, Zn, and Al triflate salts in the aprotic solvent is somewhat limited, only 0.1 M solutions could be prepared.

All the procedures involving materials sensitive to humidity were run in a dry room (relative humidity < 1%) or in a helium-filled drybox (H_2O < 1 ppm).

Results

Contrary to previous results with V_2O_5 xerogel (and other vanadium oxide hosts), we found that Mg^{2+} , Al^{3+} , and Zn^{2+} insertion is facile in the aerogel and that up to 4 equiv of Mg^{2+} , 3.33 equiv of Al^{3+} , and 2.5 equiv of Zn^{2+} may be inserted per mole of V_2O_5 (ARG). Formal reduction by 4 equiv/mol of V_2O_5 corresponds to reducing pentavalent vanadium to the trivalent state and is analogous to insertion of 4 equiv of Li^+ ions.^{3,4} To our knowledge this is the highest intercalation capacity for Mg^{2+} , Al^{3+} , and Zn^{2+} ever reported for any vanadium oxide host. It confirms that the aerogel is an excellent and versatile host for polyvalent as well as for monovalent metal cations.

Chemical analysis (Galbraith Laboratories) further showed that the amount of water present in the intercalated materials was unchanged, i.e., there was no reaction between the organometallic reagents and the chemically bound water in the aerogel. Such a result is in agreement with the one obtained for chemically and electrochemically lithiated V_2O_5 aerogel samples. The water does not react with the intercalated lithium as indicated by the full reversibility of the lithium intercalation reaction.

To characterize the thermodynamic properties of the $M_xV_2O_5$ aerogel, we measured the OCP of the intercalated dry powders in electrochemical cells, and the results are plotted in Figure 2. Also plotted for com-

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Table 1. Two-Electrode Cell Cathode and Anode Compositions before and during the Cyclic Voltammetry Tests^a

cell		first cycle (end of cathodic sweep)		steady cycle (end of cathodic sweep)		steady cycle (end of anodic sweep)	
cathode	anode	cathode	anode	cathode	anode	cathode	anode
V ₂ O ₅	Mg _{0.62} V ₂ O ₅	Mg _{0.3} V ₂ O ₅	Mg _{0.29} V ₂ O ₅	Mg _{0.27} V ₂ O ₅	Mg _{0.38} V ₂ O ₅	Mg _{0.13} V ₂ O ₅	Mg _{0.53} V ₂ O ₅
V ₂ O ₅	Zn _{0.52} V ₂ O ₅	Zn _{0.21} V ₂ O ₅	Zn _{0.36} V ₂ O ₅	Zn _{0.2} V ₂ O ₅	Zn _{0.37} V ₂ O ₅	Zn _{0.08} V ₂ O ₅	Zn _{0.51} V ₂ O ₅
V ₂ O ₅	Al _{1.33} V ₂ O ₅	Al _{0.81} V ₂ O ₅	Al _{0.62} V ₂ O ₅	Al _{0.54} V ₂ O ₅	Al _{0.86} V ₂ O ₅	Al _{0.25} V ₂ O ₅	Al _{1.11} V ₂ O ₅

^a First cycle and steady cycle compositions are calculated from the charge at the end of the cathodic and/or anodic sweeps.

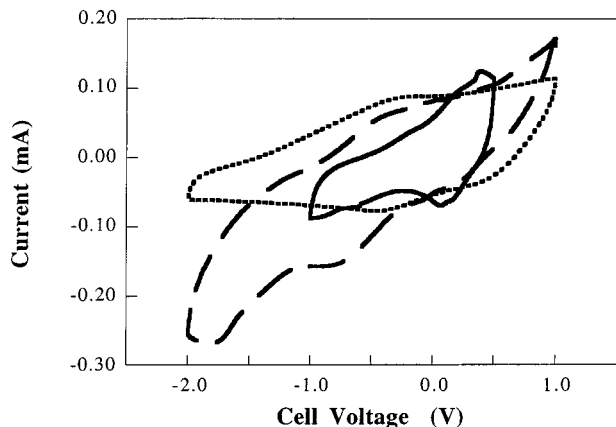


Figure 3. Two-electrode cyclic voltammograms of the Mg_{0.62}V₂O₅ (dotted curve), Zn_{0.52}V₂O₅ (solid curve) and Al_{1.33}V₂O₅ (dashed curve). The chemically intercalated materials were used as source-sink of the polyvalent cations. Bare V₂O₅ aerogel pellets were used as working electrode. Electrolyte: 0.1 M Mⁿ⁺(CF₃SO₃)_n in propylene carbonate; T: 25 °C; sweep rate: 0.1 mV/s.

parison are the equilibrium potentials of Li_xV₂O₅ aerogels, also vs pure lithium metal. The points for the polyvalent cation intercalation consistently lie within a few hundred millivolts of the lithium curve. Because all the curves are so similar, one concludes that the primary factor that controls the equilibrium voltage is the redox state of the host material (vanadium oxide). The nature of the cation guest is of lesser importance. We expect to explore this tentative conclusion by further studies now underway.

In Figure 3 are illustrated the cyclic voltammograms (steady cycle) of the two-electrode cells in which the chemically intercalated samples were used as counter electrode and virgin V₂O₅ aerogel was used as the working electrode. As a result of the absence of a reference electrode in the cells, further accentuated by the very low conductivity of the electrolytic solutions, the shapes of the voltammograms are not well defined. Nevertheless, the broad peaks in the cyclic voltammetry experiments indicate a net movement of charge between the two electrodes. The amounts of polyvalent cations exchanged in the first cycle and in a steady-state cycle are reported in Table 1. This evidence clearly confirms that the polyvalent cations can be reversibly moved from one electrode to the other with a rocking chair mechanism. Virgin V₂O₅ aerogel can act as host for the intercalation of polyvalent cations and chemically intercalated V₂O₅ aerogels can act as source of the polyvalent cations.

Discussion and Conclusions

From Figure 2, it is possible to estimate the specific energy for insertion of the polyvalent cations into V₂O₅ (ARG). For example, in the case of magnesium, if the potential is corrected for the Mg²⁺/Mg–Li⁺/Li potential difference (assumed to be about 0.8 V), the specific energy is calculated to be 1200 W h/kg for intercalation of 4 equiv of Mg²⁺, based on the mass of the active cathode material. Similar calculations for Al³⁺ and Zn²⁺ were carried out by assuming the respective equilibrium potentials of the metals are 1.3 and 2.2 V, respectively, vs Li⁺/Li. For 3.33 equiv of Al³⁺ intercalation, the specific energy is estimated to be 750 W h/kg. For 2.5 equiv of Zn²⁺ intercalated, the specific energy is estimated to be 270 W h/kg. These specific energies may be compared to the experimental specific energy of 1600 W h/kg for intercalation of 4 Li⁺ into V₂O₅ (ARG) reported earlier.^{3,4} In all of the systems, the intercalation is reversible, and further study is underway to explore this.

As a final note, we propose that there are at least two reasons why the V₂O₅ (ARG) has high experimental capacities for the polyvalent cations. First, the highly porous ARG has small pore wall dimensions (of the order of 10–50 nm) and thus small diffusion distances in the solid. This leads to rapid intercalation into the solid host (diffusion effect) and is probably a major reason for the great enhancement over the xerogel where diffusion distances (defined by the particle size of the xerogel powder) are often 10 μm or larger. That is, previous measurements of low intercalation capacity may have been influenced by kinetic limitations. The increased interlayer spacing in the aerogel probably facilitates cation insertion as well and alters the site energy for polyvalent cations in the host (thermodynamic effect) which promotes higher capacity.

The present results provide a firm basis to suggest that high-energy intercalation batteries based on Mg²⁺, Al³⁺, or Zn²⁺ may be attainable. Further, hydrated electrolytes are not needed in order to obtain high insertion capacities. Combining this with the availability and relatively low cost of the metals, and the increased safety, as compared to lithium, the systems could be viable alternatives to lithium-based systems. Further work is in progress to determine the reversibility of intercalation and other properties such as stability, which must be established before such systems would be practical.

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