

Metal Oxide Composites for Lithium-Ion Battery Anodes Synthesized by the Partial Reduction Process

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A thermochemical process based on the partial reduction of mixed oxides is used to create ultrafine metal-ceramic composites for Li-ion battery electrodes. Mixed oxides containing a more noble metal selected to be capable of alloying with lithium at potentials useful as a Li-ion battery anode are partially reduced to form electrochemically active metal-ceramic composites. Experiments show the differences in microstructure obtained in systems with slow oxygen diffusion (SbVO₄, AgVO₃, and Ag₂V₄O₁₁), fast oxygen diffusion (Sb₂Mn₂O₇ distorted fluorite), and microphase separation (Sn_{0.5}Ti_{0.5}O₂ rutile). Materials are characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and scanning transmission electron microscopy, and electrochemical tests are presented. Reversible charge capacities of 200-350 mAh/g (1100-2200 mAh/cm³) have been obtained in experiments to date.

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Increased demand for high density portable energy storage has driven searches for new storage materials with improved performance. Several Li-metal alloy systems have been investigated as alternatives to the carbon negative electrode in Li-rechargeable batteries, due to their high theoretical energy densities.¹⁻³ However, due to large volume changes occurring upon Li insertion and removal during cycling which lead to mechanical failure of the electrode, the cyclability of bulk metal alloys is poor.

Many efforts have been directed toward improving the cycling stability of these metal electrodes. The development of tin oxidecontaining glass anodes and the mechanistic investigation of this class of materials have shown that improved cyclability is possible if the metal phase is prepared as ultrafine particulates.⁴⁻⁶ These oxides offer higher volumetric capacity than carbon (>1800 mAh/cm³) and can exhibit good cyclability, but a major limiting factor is the large irreversible capacity loss during the first cycle, due to irreversible lithium consumption upon initial electrochemical reduction of thin oxide to tin metal prior to lithium alloying.⁵ Reduction of the first-cycle irreversibility while maintaining good cyclability has been described for composites containing ultrafine dispersions of lithium-active metals produced by mechanical milling or multiphase active metal systems.⁶⁻⁸ These studies suggest that metal anodes may be viable if stabilized fine dispersions of lithium-active metals are attained.^{2-3,7-9}

Here the partial reduction of several mixed oxides has been explored as an alternative approach to synthesizing metal-ceramic nanocomposites with reduced first-cycle irreversibility loss, and in which phase and volume changes during lithium insertion and removal can be accommodated. This approach allows tailored phase assemblages and microstructures to be prepared using simple, economical thermochemical processes and inexpensive starting materials. While partially reduced oxides have previously been investigated for possible applications, including selective absorption of solar energy, optical data storage, and toughening of ceramics,¹⁰⁻¹⁶ we show that this method can also be used to synthesize electrochemically active materials in several systems. Experiments are discussed for ternary oxides in the systems Sb-V-O, Sb-Mn-O, Ag-V-O, and Sn-Ti-O.

Partial Reduction Approach

A general introduction to the partial reduction approach for creating metal-metal oxide composite Li-storage materials is given elsewhere.¹⁷ The main concepts are as follows. Partial reduction is a thermochemical process in which a ternary or higher-order oxide (or nitride, sulfide) is subjected to conditions that reduce the most noble metal(s) but leaves the less noble metal(s) in an oxidized form¹⁰

$$\mathrm{Me}_{a}^{\mathrm{I}}\mathrm{Me}_{b}^{\mathrm{II}}\mathrm{O}_{c} \xrightarrow{\mathrm{partially}} a\mathrm{Me}^{\mathrm{I}} + \mathrm{Me}_{b}^{\mathrm{II}}\mathrm{O}_{y} + (c - y)/2 \mathrm{O}_{2} \quad [1]$$

Here Me^{I} is more noble than Me^{II} (Me^I lies above Me^{II} on the Ellingham diagram). Depending on the starting composition, the relative diffusion rates of oxygen and the cations, and the phase makeup (single or multiphase) of the material, either internal reduction wherein the reduced species precipitates inside an oxide matrix, or external reduction wherein the reduced metal forms at the outer surface, can occur.¹⁰

For use as a lithium-storage electrode, our objective is to produce fine particles of a lithium-active metal, Me^{I} , enclosed within or dispersed among particles of a metal oxide matrix $Me^{I}_{b}O_{y}$. The matrix itself may or may not be lithium active but should be a good electronic and lithium-ion conductor. For high energy density as an anode, alloying at a low voltage of Me^{I} with Li and a high Li/Me^I ratio are also preferred.

One expects that the first-cycle irreversibility of the electrode can be reduced in such a composite compared to an oxide that is electrochemically reduced since the displacement reactions forming Li_2O as a by-product upon first lithium insertion⁵ can be avoided. These displacement reactions are typically irreversible or poorly reversible. Direct lithiation of the metal phase is possible after partial reduction

$$(\mathrm{Me}^{\mathrm{I}}-\mathrm{Me}^{\mathrm{II}})_{a}\mathrm{O}_{b} \xrightarrow[\mathrm{reduced}]{\mathrm{partially}} \mathrm{Me}^{\mathrm{I}} + \mathrm{Me}_{b}^{\mathrm{II}}\mathrm{O}_{y} \xrightarrow{x\mathrm{Li}} \mathrm{Li}_{x}\mathrm{Me}^{\mathrm{I}} + \mathrm{Me}_{b}^{\mathrm{II}}\mathrm{O}_{y}$$

$$[2]$$

Furthermore, ultrafine metal particles, which appear to better tolerate cyclic volume changes than coarser particles or bulk metal,^{3,8,18} can be produced. Internal reduction where metal particles are embedded in the oxide matrix can prohibit coarsening of the metal particles during heat-treatment, and very fine particle sizes on the order of a few nanometers have been obtained in previous studies.¹⁰⁻¹⁶ The fact that almost all metal oxides undergo volume shrinkage upon reduction can be advantageous by providing room for the subsequent expansion of the metal upon lithiation. Finally, a microstructure whereby the lithium-active metal is embedded within a metal oxide matrix can improve the chemical compatibility between the storage material and the electrolyte system, especially since passivating layers are well known to form between metal electrodes and liquid electrolytes. Transition-metal oxides are among the

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Table I. Examples of mixed metal oxides that have been partially reduced to form metal-ceramic composite anodes. Their structure, composition, and transport characteristics are relevant to the microstructures obtainable through thermochemical reduction.

Compound	Structure	Diffusivity	Observed characteristic and interpretation
SbVO ₄	Rutile	$D_{ ext{cations}} > D_{ ext{oxy}}$ $D_{ ext{v}^{3+}} > D_{ ext{Sb}^{5+}}$	External reduction as expected
$\mathrm{Sb}_{2}\mathrm{Mn}_{2}\mathrm{O}_{7}$	Distorted fluorite	$D_{\rm oxy} > D_{\rm cations}$	Internal reduction
AgVO ₃	Perovskite	$D_{ m cations} > D_{ m oxy}$ $D_{ m Ag^{1+}} > D_{ m v^{5+}}$	External reduction due to high Ag/V ratio
$Ag_2V_4O_{11}$	Bronze (corner-shared octahedra)	$D_{ m cations} > D_{ m oxy}$ $D_{ m Ag^{1+}} > D_{ m v^{5+}}$	Internal reduction
(Sn,Ti)O ₂	Rutile	$D_{\text{cations}} > D_{\text{oxy}}$	Internal reduction due to phase confinement

most attractive candidates for the host metal oxide $Me_b^HO_y$ since most are chemically compatible with organic liquid electrolytes and also have high electronic and lithium ionic conductivity.

Since the electrochemical performance of such composites, especially upon extended cycling, depends critically on the microstructure that is obtained, within the general approach of partial reduction, we have also identified three specific strategies for obtaining fine dispersions of the metal within an oxide matrix: (*i*) in oxides with low oxygen diffusivity, the concentration and relative diffusivity of the lithium-active metal can be selected to obtain internal *vs.* external precipitation of the reduced metal;¹⁰ (*ii*) systems of high oxygen diffusivity, for which internal reduction is always expected, can be selected; and (*iii*) phase separation can be conducted prior to reduction, in order to confine the reduced metal phase. In this paper, we illustrate these approaches using several examples.

Selected Systems

Table I lists example systems we have investigated. Each system has different structural, composition, and transport characteristics which result in different microstructures and electrochemical characteristics.

 $SbVO_4$ and $Sb_2Mn_2O_7$.—Sb can alloy up to three Li per Sb atom at a voltage plateau of 0.94-0.96 V¹⁹ relative to Li metal. Interestingly, the molar volumes of Sb₂O₅ and Li₃Sb are almost equal, resulting in nearly zero volume change upon reducing the oxide to Sb metal followed by lithiation to Li₃Sb. We compare the starting oxides SbVO₄ and Sb₂Mn₂O₇ because of their different crystal structures and transport characteristics. SbVO₄ has the rutile structure in which cation diffusion is expected to be more rapid than oxygen diffusion; hence, the kinetics of partial reduction analyzed by Schmalzried and Backhaus-Ricoult¹⁰ should apply. Due to the high Sb fraction, external reduction may occur. This compound has been widely used in catalytic applications.²⁰ In contrast, Sb₂Mn₂O₇ has the distorted fluorite structure²¹ in which oxygen diffusion should be much more rapid than cation diffusion once some reduction occurs, resulting in oxygen vacancies. In this case, internal reduction is expected as long as the matrix remains intact. Some results on this system have already been reported in Ref. 17. Here we present additional results showing how control of the starting oxide particle size can be used to increase the fraction of internal metal. Analyses of the composite morphology before and after cycling have also been conducted.

 $AgVO_3$ and $Ag_2V_4O_{11}$.—Lithium is reported to alloy with Ag to form compounds LiAg, Li₁₀Ag₃, and Li₁₂Ag,²² thereby yielding



Figure 1. XRD patterns of (a) SbVO₄ partially reduced at 400°C for 4 h in H_2 and (b) Sb₂Mn₂O₇ partially reduced at 360°C for 18 h in H_2 .

potentially high storage capacities. In electrochemical tests, Ag alloys with Li at a low voltage of ~0.02-0.1 V for low concentrations;²³ more highly lithiated alloys have not been obtained. Both AgVO₃ and Ag₂V₄O₁₁ are compounds in which oxygen diffusion is expected to be slow relative to cation diffusion, but the lower Ag concentration in the latter should promote internal reduction.¹⁰ AgVO₃ is available commercially, and Ag₂V₄O₁₁ is a well-known cathode material for primary lithium cells used in medical implant applications.²⁴ After partial reduction, the vanadium oxide matrix is attractive due to its high lithium-ion and electronic conductivity.

 $Sn_{1-x}Ti_xO_2$.—(Sn,Ti)O₂ was studied as an example of metal confinement due to phase separation. SnO₂ lies well above TiO₂ on the Ellingham diagram and can be preferentially reduced. Sn is a wellstudied metal anode that can alloy up to 4.4 Li per Sn, while TiO₂ is known to have good ionic and electronic conductivity.²⁵ While a complete rutile solid solution of TiO2 and SnO2 can be achieved at high temperatures ($T > 1430^{\circ}$ C for the equimolar composition),²⁶ at lower temperatures there is a miscibility gap that is nearly symmetrical in composition. Within the spinodal regime, finely divided lamellar microstructures with layers as fine as 20 nm thick, alternatively rich in SnO₂ and TiO₂, can be obtained.^{27,28} Two-phase microstructures of varying length scales can be created, within which the SnO₂-rich phase can be preferentially reduced to Sn metal. Doping influences both decomposition kinetics^{27,28} and electrical properties; most subvalent cations in TiO2 form deep acceptor levels resulting in electronically insulating oxides at room temperature, while supervalent cations tend to form shallow donor levels yielding good electronic conductivity.^{25,29} Therefore, both microstructure and electronic conductivity can be widely manipulated in this system through control of composition and processing conditions.



(a)





Figure 4. Voltage *vs.* capacity curve of (a) Sb-V₂O₃ produced by partial reduction of SbVO₄ (400°C for 4 h in H₂), tested at 10 mA/g, and (b) Sb-MnO produced by partial reduction of Sb₂Mn₂O₇ (360°C for 18 h in H₂), tested at 14 mA/g.

Experimental

Figure 2. SEM images of (a) partially reduced SbVO₄ (400°C for 4 h in H₂) and (b) partially reduced Sb₂Mn₂O₇ (360°C for 18 h in H₂). Coarse externally precipitated Sb is seen for the SbVO₄ derived sample, while much finer internal precipitates of Sb are found for Sb₂Mn₂O₇, in which oxygen diffusion is much faster than cation diffusion.

SbVO₄, Sb₂Mn₂O₇, and Ag₂V₄O₁₁ were prepared using solidstate reaction processes beginning with reagent grade oxides or carbonates. SbVO₄ was prepared by ballmilling a 1:1 molar ratio of Sb₂O₃ (99.3% Alfa Aesar) with V₂O₅ (99.6% Aldrich) in a polypropylene bottle using Teflon balls for 24 h. The mixture was then fired



Figure 3. SEM image of partially reduced $Sb_2Mn_2O_7$ (420°C for 24 h in H₂) with initially large starting $Sb_2Mn_2O_7$ particle size and its cross-sectional back-scattering SEM image, showing internally precipitated Sb metal.

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Figure 5. Capacity *vs.* cycle number. (a) Sb-V₂O₃ sample with large external Sb precipitates (0.5-1.5 V, 10 mA/g). Note the rapid fade in the first few cycles. (b) Sb-MnO (sample from Fig. 2b) with finer external precipitates as well as internally reduced Sb (0.7-1.3 V, 14 mA/g). (c) Sb-MnO (sample from Fig. 3) with predominantly internal Sb particles (0.7-1.3 V, 6 mA/g).

in air at 700°C for 24 h, resulting in a single phase of $SbVO_4$. $Sb_2Mn_2O_7$ was prepared by ballmilling a 1:2 molar ratio mixture of

 Sb_2O_3 (99.3% Alfa Aesar) and MnCO₃ (99.9% Alfa Aesar), and then calcining and reacting in air at 600°C for 7 h, 650°C for 4 h, 750°C for 5.5 h, and 1100°C for 21 h.

 $Ag_2V_4O_{11}$ powder was prepared by ballmilling a 1:2 molar mixture of Ag_2O (99% Alfa Aesar) and V_2O_5 (99.6% Aldrich). Singlephase $Ag_2V_4O_{11}$ was obtained after reacting the mixture in O_2 atmosphere at 500°C for 10 h. The AgVO₃ starting powder was purchased from Aldrich (Aldrich Chemical Co., Milwaukee, WI).

Phase-separated SnO2-TiO2 composites were obtained by first synthesizing a (Sn,Ti)O₂ solid solution powder and then carrying out thermal decomposition. The compositions studied had a 1:1 molar ratio of Sn:Ti, to which Al^{3+} (0.8 mol %) and Ta^{5+} (0.6-1.0 mol %) were added as the acceptor and donor dopants, respectively, to influence decomposition and electrical properties. The starting powder was prepared via either a coprecipitation²⁸ or a solid-state reaction method. In the solid-state reaction method, stoichiometric amounts of SnO₂ (99.9% Alfa Aesar) and TiO₂ (99.9% Alfa Aesar) doped with Al(OH)3 (Alfa Aesar) or Ta2O5 (99.993% Puratonic) were ballmilled as described previously, then heated in air to 1475°C, a temperature above the miscibility gap maximum (1430°C), for 12 h to obtain a solid solution oxide. For starting powder prepared by either method, decomposition heat-treatments were subsequently carried out between 900 and 1000°C for 12-880 h to allow phase separation. The rate of phase separation is highly sensitive to composition and temperature in this system. X-ray diffraction (XRD) was used to confirm that phase separation had occurred prior to partial reduction in each instance.

For partial reduction, a small amount of each powder (\sim 0.4-2 g) was heated in an alumina boat (powder depth ~ 2 mm) in a tube lined furnace (temperature and atmospheric conditions are given in the Results and Discussion section for each material). Both buffered CO/CO₂ gas mixtures and unbuffered pure H₂ gas at 1 atm total pressure were used. For the CO/CO2 gas mixture, temperature and oxygen activity can be selected to reduce only the more noble metal. For hydrogen gas, although the specific oxygen partial pressure could not be determined, we could carry out the reduction process at low temperatures (<500°C) without the deposition of carbon observed for CO/CO₂. XRD (Rigaku RU300, Cu Kα radiation) and weight loss were conducted for each sample before and after partial reduction heat-treatments to determine the phases present and the extent of reduction. For brevity, the detailed data are not included here but are available in Ref. 30. JEOL 2000FX and 2010FX transmission electron microscopes (TEM), a Fisons HB603 scanning transmission electron microscope (STEM), a Philips XL30 environmental scanning electron microscope, and a JEOL JSM-6320FV field emission gun scanning electron microscope were used to characterize the sample microstructures and identify phases.

Electrodes consisting of 70-88 wt % of the sample, 5-10 wt % carbon additive (Super P, Chemetals Inc.; acetylene black, 99.9%, Alfa Aesar; or graphite, 1-2 µm, Aldrich), and 10-20 wt % of polyvinylidene fluoride binder (Aldrich) were prepared. These were mixed with γ -butyrolactone solvent (98%, Alfa Aesar) and either cast on a sheet of Cu foil, or dried and then pressed at 4000 kg/cm³ into 1/4 in. diam pellets. All electrodes were assembled in stainless steel cells using Li foil (Alfa Aesar) as the reference electrode, and ethylene carbonate:dimethyl carbonate (1:1 by weight) with 1 M LiPF₆ (EM Science) as the electrolyte, and Celgard 2400 as the separator. Cycling was conducted at room temperature. The Super P carbon additive made a significant contribution to the first-cycle irreversible capacity loss and reversible capacity of the electrodes. When formulated into electrodes and tested separately, up to 550 mAh/g of carbon and up to 80 mAh/g irreversible capacity was seen on the first discharge at 0.7-1.3 V. The capacity data was corrected by subtracting the capacity contribution of the added carbon from the total electrode capacity.



Figure 6. Cross-sectional backscattering SEM image of the Sb-MnO composite after electrochemical cycling (50 cycles between 0.7 and 1.3 V). The microstructure of Sb embedded in MnO is retained.

Results and Discussion

 $SbVO_4$ and $Sb_2Mn_2O_7$.—Partial reduction was successfully carried out at very low temperatures; complete reduction of the antimony oxide fraction to Sb metal could be accomplished at temperatures as low as 400°C (4 h, H₂) for SbVO₄, and 360°C (18 h, H₂) for Sb₂Mn₂O₇. Figure 1a and b (from Ref. 17) show XRD patterns of the partially reduced SbVO₄ and Sb₂Mn₂O₇, respectively. SEM and TEM analyses showed a dramatic difference in Sb precipitate size between the two. Reduced SbVO₄ showed external Sb metal



Figure 7. XRD patterns of (a) AgVO₃, partially reduced at 360°C for 6 h in H_2 , and (b) Ag₂V₄O₁₁, partially reduced at 500°C for 4 h in H_2 .



Figure 8. (a) STEM image of internally precipitated Ag for $Ag_2V_4O_{11}$ partially reduced at 500°C for 4 h in H₂. (b) Cycling data for the partially reduced $Ag_2V_4O_{11}$ (20 mA/g).

precipitates of octahedral morphology as large as 20 μ m mixed with vanadium oxide phase, while the reduced Sb₂Mn₂O₇ exhibited much finer Sb particles, ranging from ~2 μ m to ~20 nm as observed by SEM and TEM analysis, mixed with MnO phase (Fig. 2a, b).¹⁷ The finer precipitate size occurred despite a longer reduction time for Sb₂Mn₂O₇. We believe that Sb metal precipitation occurs internally in the distorted fluorite due to its high oxygen diffusivity, causing Sb coarsening to be inhibited. In contrast, external reduction appears to occur throughout for the slow oxygen diffusion system SbVO₄, leading to coarse metal. For Sb₂Mn₂O₇, even though the precipitated metal is primarily internal, a certain amount of Sb lying within a characteristic diffusion length of the surface can diffuse to the surface and form external precipitates of Sb metal.

To obtain samples with a finer and higher fraction of Sb internal precipitates, the Sb₂Mn₂O₇ particle size prior to partial reduction was increased through thermal coarsening. This lowers the specific surface area and is expected to decrease the fraction of external precipitates. The as-synthesized Sb₂Mn₂O₇ was further heat-treated for various times and temperatures, after which the particle size was examined using SEM. Here we present results for heat-treatment in air at 1300°C for 8 h. A significant increase in the average particle size from <1 μ m in the starting material to 6.5 μ m after coarsening

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Figure 9. Bright-field TEM images of doped $Sn_{0.5}Ti_{0.5}O_2$. (a) 0.8 mol % Al-doped phase separated at 900°C, 12 h, and (b) partially reduced at 360°C, 15 h in H_2 . (c) 1 mol % Ta-doped composition phase separated at 1000°C, 325 h, and (d) partially reduced at 450°C, 24 h in H_2 .

was observed. The coarsened $Sb_2Mn_2O_7$ was then subjected to partial reduction at 420°C for 24 h in H₂. SEM images of the coarsened oxide and partially reduced Sb-MnO composite (Fig. 3) show that a high fraction of Sb internal precipitates is obtained.

Figures 4a and b show typical voltage profiles for the Sb-V₂O₃ and Sb-MnO composites, respectively. The average voltage between charge and discharge plateaus was ~ 0.97 V, and closer examination revealed two closely spaced plateaus upon discharge, corresponding to the formation of Li₂Sb and Li₃Sb, respectively.¹⁹ Upon cycling, the coarse-grained Sb-V₂O₃ composite behaves like a mixture of the two phases without a tailored microstructure. The composite has an initial capacity of 415 mAh/g that is close to the theoretical value of a 1:1 molar ratio of Sb: V_2O_3 (409 mAh/g), assuming V_2O_3 to be inactive in this voltage range. However, rapid capacity fade in the first several cycles was observed for the coarse Sb metal in this sample (Fig. 5a). The Sb₂Mn₂O₇-derived material with its finer metal dispersion exhibits much better cyclability (Fig. 5b). The sample with a still higher fraction of fine internal Sb precipitates, shown in Fig. 3, exhibited even better capacity retention (Fig. 5c). These cells did show lower coulombic efficiency and a surprising feature of sudden fade after about 20 cycles (Fig. 5b, c). Further investigation indicated that the sudden capacity fade was a cell failure and not an intrinsic property of the tested material. After the sudden capacity fade of cell Sb-MnO no. 1 at the 20th to 25th cycle and Sb-MnO no. 2 at the 20th to 22nd cycle, the cells were disassembled and reassembled using a new lithium electrode and electrolyte. The charge (lithium extraction) capacities were then mostly restored. Furthermore, the cumulative inefficiencies found in these samples are much larger than the irreversible storage capacities possible from the materials in the electrode. The inefficiency also increases again after the rebuilding of the cells (Fig. 5b, c). This indicates that the coulombic inefficiency cannot be attributed to the tested material alone but to some other side reaction due to the Li metal electrode or the electrolyte, such as solid electrolyte interphase (SEI) formation or electrolyte decomposition.

SEM examination of the microstructure of the internally reduced Sb-MnO composite after electrochemical cycling reveals that the initial morphology of Sb metal embedded in the MnO matrix was retained (Fig. 6), although some fracturing of the matrix does occur. We attribute the improved capacity retention upon cycling of this material to the preservation of the internal reduction morphology, which helps to maintain connectivity between the active metal and the oxide matrix through cyclic volumetric expansion and contraction of the metal. In a separate study,³¹ we showed that Sb metal powder cycled in the same electrolyte system undergoes systematic disintegration into nanocrystalline metal particles. This is clearly avoided when the Sb metal is contained within an oxide matrix, as in the internally reduced Sb-MnO composites.

The theoretical charge capacity for Sb-MnO obtained by reducing $Sb_2Mn_2O_7$ is 417 mAh/g (2570 mAh/cm³, assuming the theo-

retical density of 6.16 g/cm³). The two Sb₂Mn₂O₇-derived samples in Fig. 5b and c show reversible capacities of \sim 300 mAh/g (1850 mAh/cm³) and ~225 mAh/g (1385 mAh/cm³), respectively. In the latter case, the reduced capacity is attributed to incomplete reduction of the Sb oxide in the starting material. This was clearly evident in the amount of weight loss and the presence of retained fluorite phase in the reduced sample observed by XRD. (From the measured weight loss before and after reduction, it was calculated that 76% of the starting Sb-O was reduced to Sb metal, assuming that every 1 mol of the partially reduced Sb₂Mn₂O₇ gives 2 mol of Sb metal and 2 mol of MnO upon reduction.) With further development, a reversible gravimetric capacity of ~350 mAh/g corresponding to a volumetric capacity of $\sim 2150 \text{ mAh/cm}^3$ should be possible for this system. The comparison between SbVO₄ and Sb₂Mn₂O₇ clearly demonstrates the influence of the structure and transport properties of the starting compound on the microstructure obtainable through partial reduction, and subsequently on the electrochemical properties.

 $AgVO_3$ and $Ag_2V_4O_{11}$.—XRD patterns showing AgVO₃ partially reduced at 360°C for 6 h in H₂ and Ag₂V₄O₁₁ reduced at 500°C for 4 h in H₂ are presented in Fig. 7. Only peaks for Ag metal are seen; the vanadium oxide is present as an amorphous phase. Externally precipitated Ag particles were observed using TEM and STEM for the partially reduced AgVO3, whereas the partially reduced Ag₂V₄O₁₁ exhibited fine internal Ag precipitates <20 nm thick within the vanadium oxide (Fig. 8a). The occurrence of internal reduction in the latter case may be due to the lower Ag concentration, as expected from Schmalzreid's model.¹⁰ Cycling data for $Ag_2V_4O_{11}$ reduced at 500°C for 4 h in H₂ are shown in Fig. 8b. The reversible capacity of \sim 50 mAh/g is close to the theoretical capacity of the composite if it is assumed that only the Ag alloys with Li, and that alloying up to one Li per Ag atom occurs. This indicates that the higher lithium alloys (Li₁₀Ag₃,Li₁₂Ag) are not formed within the range 0.005-2 V (to our knowledge, this is the first time this has been demonstrated). A large first-discharge capacity is also observed in this instance, which is probably due to electrochemical activity of the highly disordered vanadium oxide phase between 1.75 and 3 V. $Ag_2V_4O_{11}$ is thus another example of a system with good cyclability achieved due to internal reduction of the metal. Note that pure Ag metal powder by itself does not cycle reversibly to the composition LiAg.³¹ However, due to the low overall charge capacity of this composite system, it was not pursued further.

(Sn_{0.5}Ti_{0.5})O₂.—Figure 9 shows TEM images of phase-separated microstructures in the Sn_{0.5}Ti_{0.5}O₂ system, showing the SnO₂-rich (dark) and TiO₂-rich (light) lamellae. The Al^{3+} doped sample has lamellar spacing of 10-20 nm after being decomposed at 900°C for 12 h in air, while the Ta^{5+} doped sample has a finer spacing of <10nm despite being decomposed at a higher temperature and longer time of 1000°C for 325 h in air. This is consistent with doping effects seen in previous studies of this material.²⁶⁻²⁸ Figure 9 also shows corresponding images after partial reduction (at 360°C for 15 h in H₂ for Al-doped samples, and 450°C for 4 h in H₂ for Ta-doped samples). Much of the reduced Sn metal is captured between TiO₂-rich platelets, at a particle size of ~ 10 nm. However, a significant fraction of the reduced Sn also formed external spherical particles with a distribution of sizes up to 0.5 µm diam. Unlike the cases of Sb and Ag, partial reduction was carried out above the melting point of Sn metal (232°C). The coarser Sn particles may have coalesced from smaller droplets or coarsened through vapor phase transport. Thus these composites contain a distribution of Sn particle sizes ranging from ~ 10 nm to ~ 0.5 µm, with a larger average size occurring in the Al-doped samples. Based on the weight loss during partial reduction, it was determined that only 33% of the total SnO₂ had been reduced to Sn metal for the Aldoped sample (partially reduced at 360°C for 15 h in H₂), and 56% for the Ta-doped sample (partially reduced at 450°C for 4 h in H₂).

1.5 1 0.5 1**d** 0 200 400 600 800 0 Capacity (mAh/g) 3 60 mA/g b) 2.5 1c 6c 2 Voltage (V) 1.5 1 0.5 1**d** 0 0 200 400 600 800 Capacity (mAh/g) 3 60 mA/g 2.5 c) 11c 1c 2 1.5



This may be due to slow reduction kinetics at the temperatures used, as well as retention of $\sim 10\%$ SnO₂ in solid solution in the TiO₂, as indicated by the equilibrium phase diagram.²⁷

Figure 10 compares the electrochemical behavior of the unreduced Al-doped sample, its partially reduced Sn-TiO₂ counterpart,

3.5

60 mA/g





Figure 11. Cycle *vs.* capacity of phase-separated unreduced, Al^{3+} doped partially reduced, and Ta^{5+} doped partially reduced ($Sn_{0.5}$, $Ti_{0.5}$)O₂. The best cyclability is found in the Ta^{5+} doped sample with fine Sn particles.

and the partially reduced Ta-doped Sn-TiO₂ composite. The unreduced (Sn,Ti)O₂ exhibits the largest first-cycle irreversibility (78%). Improvement in the first-cycle irreversibility was observed for both of the partially reduced samples (64% for Al-doped and 55% for Ta-doped samples). We interpret most of the irreversibility as being due to the electrochemical reduction of the residual SnO₂ to Sn. SEI formation probably also contributes to the irreversible capacities observed during the first cycle since the capacity loss is much larger than the unreduced SnO₂ alone can produce. The larger plateau at ~1 V in the unreduced sample (Fig. 10a) is consistent with the reduction of SnO₂ by Li,⁶ and the charge capacities were lower than the theoretical value of 594 mAh/g (3360 mAh/cm³) expected for Sn_{0.5}Ti_{0.5}O₂, which has been fully reduced to a 1:1 molar ratio of Sn:TiO₂.

For the Al-doped composition, both the starting oxide and the partially reduced composite exhibit poor cyclability, as seen in Fig. 10a and b. The rapid capacity fade is attributed to most of the reduced Sn being in the form of coarse particles. Note also that a large polarization develops during the first few cycles. In comparison, the Ta-doped sample exhibits lower first-cycle irreversibility, better capacity retention, and lower polarization (Fig. 10c). The lower polarization compared to Fig. 10b is attributed to the higher electronic conductivity of donor-doped TiO₂.^{25,29} Upon narrowing the voltage range of the Ta-doped sample to 0.3-1.2 V, a decrease in capacity from 300 to 200 mAh/g (1000 mAh/cm³) was seen, but the cyclability further improved (Fig. 11). After about 50 cycles, the capacity stabilized at ~100 mAh/g (Fig. 12). The earlier cycles appear to cause the systematic loss of capacity from larger Sn particulates, while the finer particles in the particle size distribution continue to cycle reversibly.

This example demonstrates the concept of partial reduction of a microphase-separated mixture of oxides to produce an electrochemically active composite. While the storage properties for the Sn-Ti-O system are not yet sufficient for practical use, we believe that further development of this concept in related systems can narrow the size distribution of active metal particles and result in improved properties.

Conclusions

The partial reduction of mixed oxides has been studied in several systems as a new approach to synthesizing electrochemically active metal-ceramic composites. By choosing oxide compounds with suitable crystal structures and active cation concentrations, fine internal dispersions of lithium-active metals can be obtained which show markedly improved resistance to cycling fade compared to coarser,



Figure 12. Extended cycling of Ta-doped $Sn-TiO_2$. Capacity drops from 200 mAh/g to 100 mAh/g at approximately 12th cycle due to coarse Sn particles with fine Sn particles continuing to cycle reversibly.

externally precipitated metal. In these materials, improved cycling is attributed to both a reduction in metal particle size and the passivation of the metal particles by the surrounding oxide matrix. While first-cycle irreversibility due to the presence of residual lithiumactive oxide phases must be improved, reversible gravimetric capacities up to 350 mAh/g and volumetric capacities up to 2000 mAh/cm³ have been demonstrated in the systems studied to date. From the processing viewpoint, this approach is attractive since inexpensive starting materials and simple, scalable, thermochemical processes can be used.

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References

- 1. D. Fauteux and P. Koksbang, J. Appl. Electrochem., 23, 1 (1993).
- 2. R. A. Huggins, J. Power Sources, 26, 109 (1989).
- 3. J. Yang, M. Winter, and J. O. Besenhard, Solid State Ionics, 90, 281 (1996).
- Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, and T. Miyasaka, Science, 276, 1395 (1997).
- 5. I. Courtney and J. Dahn, J. Electrochem. Soc., 144, 2045 (1997).
- O. Mao, R. L. Turner, I. A. Courtney, B. D. Fredericsen, M. I. Buckett, L. J. Krause, and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2, 3 (1999).
- G. M. Ehrlich, C. Durand, X. Chen, T. A. Hugener, F. Spiess, and S. L. Suib, J. Electrochem. Soc., 147, 886 (2000).
- J. Yang, Y. Takeda, N. Imanishi, and O. Yamamoto, J. Electrochem. Soc., 146, 4009 (2000).
- 9. I. Courtney and J. R. Dahn, J. Electrochem. Soc., 144, 2942 (1997).
- 10. H. Schmalzried and M. Backhaus-Ricoult, Prog. Solid State Chem., 22, 1 (1993).
- 11. J. Narayan and Y. Chen, Philos. Mag. A, 49, 475 (1984).
- K. M. Ostyn, C. B. Carter, M. Koehne, H. Falke, and H. Schmalzried, J. Am. Ceram. Soc., 67, 679 (1984).
- R. Subramanian, E. Üstündag, S. L. Sass, and R. Dieckmann, *Mater. Sci. Eng.*, A, 195, 51 (1995).
- E. Üstündag, R. Subramanian, R. Dieckmann, and S. L. Sass, Acta Metall. Mater., 43, 383 (1995).
- J. A. Smith, P. Limthongkul, L. Hartsuyker, S. Y. Kim, and S. L. Sass, J. Appl. Phys., 83, 2719 (1998).
- 16. D. L. Ricoult and H. Schmalzried, J. Mater. Sci., 22, 2257 (1987).
- 17. P. Limthongkul, H. Wang, and Y.-M. Chiang, Chem. Mater., 13, 2397 (2001).
- 18. R. A. Huggins and W. D. Nix, *Ionics*, **5**, 57 (2000).
- 19. J. Wang, I. D. Raistrick, and R. A. Huggins, J. Electrochem. Soc., 133, 457 (1986).
- 20. G. Centi, F. Marchi, and S. Perathoner, Appl. Catal., A, 149, 225 (1997).
- 21. H. G. Scott, J. Solid State Chem., 66, 171 (1987).
- 22. P. M Hansen, Constitution of Binary Alloys, McGraw-Hill, New York (1958).

- 23. J. O. Besenhard, J. Yang, and M. Winter, J. Power Sources, 87, 68 (1997).
- C. A. Vincent and B. Scrosati, *Modern Batteries*, p. 121, John Wiley & Sons, New York (1997).
- 25. J. F. Baumard and E. Tani, J. Chem. Phys., 67, 857 (1977).
- R. S. Roth, T. Negas, and L. P. Cook, *Phase Diagrams for Ceramists*, Vol. 4, G. Smith, Editor, The American Ceramic Society, Westerville, OH (1981).
- 27. T. C. Yuan and A. V. Virkar, J. Am. Ceram. Soc., 71, 12 (1988).
- H. Maruyama, Y.-M. Chiang, M. Kawamoto, Y. Seki, S. Arakawa, K. Kikuta, and S. Hirano, *Ceramic Transactions*, Vol. 24, T. O. Mason and J. L. Routbort, Editors, p. 367, The American Ceramic Society, Westerville, OH (1991).
- 29. J. A. S. Ikeda and Y.-M. Chiang, J. Am. Ceram. Soc., 76, 2437 (1993).
- 30. P. Limthongkul, Ph.D. Thesis, MIT, Cambridge, MA (2002).
- P. Limthongkul, E. Jud, and Y.-M. Chiang, Paper 255 presented at The Electrochemical Society Meeting, San Francisco, CA, Sept 2-7, 2001.