Novel Path to Nanocomposite Cathodes and Anodes Enabling High Power Li-ion and Next-Generation Batteries

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Abstract:
A novel, scalable method for the kinetically controlled catalytic synthesis of nanocomposite cathodes and anodes uniquely enabling high power, high-voltage lithium ion and next-generation batteries for pulse-power applications with enhanced stability is presented by LifeCel Technology. A nanocomposite BaSrTiO$_3$ thin-film ceramic under cooperative development with Quallion offers internal protection against thermal runaway.

Synopsis:
New materials are needed to radically transform the efficiencies of energy harnessing, transduction, storage and delivery. To help address this need, we are investigating the mechanism and optimizing the usefulness of a new, biologically inspired, low cost, low temperature method we developed for the kinetically controlled catalytic synthesis of nanostructured materials for energy applications. This novel materials synthesis method is low-cost, low temperature, scalable, and uses no polluting chemicals. In addition to the near-term application for the improvement of batteries and related energy technologies, the broader impact of these developments includes a deeper fundamental understanding of the factors governing the control of nanoscale synthesis, assembly and performance of a wide range of semiconductors and other valuable inorganic materials. Improvement of fuel-cell efficiency requiring 30% less platinum than current commercial cells has thus been demonstrated.

Kinetically Controlled Catalytic Nanofabrication:
We translated the biomolecular mechanism of synthesis of silica and related metal oxides that we discovered to a robust new methodology, without the use of organic molecules, capable of producing nanostructurally controlled metalloid and metal oxide semiconductors and related materials for improved efficiency of energy generation, transduction, storage and use (Schwenzer et al., 2006, 2009, 2010; Brutchey and Morse, 2006; Schwenzer and Morse, 2008; Nielson et al., 2009, 2011a,b; Tao et al., 2010; Niesz et al., 2011; ). This method uses vapor diffusion of a catalyst through a gas-liquid interface to provide *kinetically and vectorially controlled catalysis*, at low-temperature, of synthesis from molecular precursors that require hydrolysis. The result is a novel low-temperature and environmentally benign method for the nanofabrication of a wide range of metal oxide, metal hydroxide and metal phosphate semiconductors (and the corresponding metals) in unique and potentially useful nanocrystalline morphologies - some of which could never have been made before - with significantly enhanced electronic performance (Schwenzer et al., 2006; Brutchey & Morse, 2006; Schwenzer & Morse,
2008). The method relies on the integrated tuning of molecular precursors and vectorially controlled catalysis, utilizing only chemical physics and highly purifiable inorganic components, with no biochemistries, biologicals or organic materials. The use of the molecular precursor and its vectorially controlled catalytic hydrolysis provide coordinate kinetic and directional control of semiconductor growth that is not available using conventional high-temperature approaches. This bio-inspired, kinetically controlled catalytic synthesis method is highly generic, yielding both free (unsupported) and supported nanostructured thin films and nanoparticles of more than 50 different metal hydroxides, oxides, phosphates and perovskites - many in morphologies that had not been achievable before. We demonstrated that the range of products can be further expanded by facile post-synthesis conversion to the nitrides and sulfides, with preservation of the nanostructured morphology. Direct reduction to the pure nanocrystalline metal also is possible. Because no organics or biochemistries are used, the method produces very high purity materials that are fully integrable with MOCVD and CMOS fabrication, as well as other conventional synthesis methodologies.

**Kinetically Controlled Catalytic Synthesis of Nanocomposite Anodes and Cathodes for High-Power Lithium Ion and Next-Generation Batteries:**

We have used the kinetically controlled catalytic synthesis method described above to inexpensively produce a nanocomposite anode for high-power lithium ion batteries consisting of nanocrystals of Sn grown by a 2-step catalytic process in situ within the pores of compliant and conductive microparticles of graphite (Fig. 1; Zhang and Morse, 2009). This composite exhibits higher energy capacity than the graphite alone, as a result of the contribution to lithium ion capacity of the metal. Exceptionally high power-density (nearly 50 % retention of capacity, with full recovery, after discharge at 50C) and high stability (cyclability) apparently are the result of the compliance of the graphite, which provides a resilient host that can accommodate the swelling and shrinking of the metal with each cycle of lithiation (alloying) and de-lithiation that accompanies each discharge and charge cycle (Zhang and Morse, 2009).

![Figure 1. High power tin-in-graphite nanocomposite anode. (left) Back-scattered electron image and EDX (energy-dispersive X-ray mapping - not shown) reveal uniform dispersion of Sn nanoparticles throughout the graphite matrix. X-ray diffraction and BET measurements (not shown) confirm that the gentle, low-temperature method preserves the essential crystallinity and high porosity of the graphite. (center) FIB cross-section and TEM show nanocrystals of tin grown in situ within the interstices of the graphite. (right) Exceptionally high rate capability with full recovery. (Zhang and Morse, 2009; submitted, 2012)](image)

Smaller Sn nanocrystals can be obtained by replacing the graphite matrix with a comparably...
conductive and compliant carbon matrix of inexpensive, mass-produced, bulk multi-wall carbon nanotubes (MW-CNTs) (Zhang and Morse, 2012). Preliminary and as-yet unoptimized results demonstrate that use of the CNT matrix yields lower heterogeneity and smaller average size (ca. 120 nm) of the final Sn nanocrystals than formed in the graphite, with nearly 50% higher energy capacity of the composite than obtained with the graphite matrix:

We also have used kinetically controlled, catalytic synthesis (albeit with different chemistry) to produce a high-power, relatively high-voltage, nanocomposite cathode for rechargeable Li-ion batteries (von Bulow et al., 2012). This cathode consists of nanocrystalline (spinel) LiMnO₄ grown in situ and intimately mixed with well-dispersed, inexpensive multiwall carbon nanotubes) (Fig. 3). This cathode operates at an average voltage of 3.9 v and exhibits exceptionally stable cyclability. It retains 96% of its original capacity after discharge at 10C, >80% capacity after discharge at the exceptionally high rate of 20C, and shows complete recovery to 100% capacity after full discharge at 50C (indicating that it suffers no damage after this exceptionally high rate of discharge) (Fig. 4).
A high-performance cathode for Li-air batteries, with significantly higher capacity and stability than its present commercial counterpart, also has been produced using our kinetically controlled catalytic synthesis method (Zhang and Morse, 2010.)

**Scalability:**

Because the kinetically controlled catalytic methods we developed are aqueous and chemical in nature, they are readily and economically scalable – in marked contrast to semiconductor vapor deposition methodologies. Thus, we have succeeded in scaling up the synthesis of the nanocomposite anode material from the 100 mg laboratory scale to the multi-100 g scale, and have developed large-scale and continuous synthesis processes for ultrapure nanocrystalline BaTiO$_3$ and BaSrTiO$_3$ (under development for battery safety applications with Quallion LLC) to produce multiple kg/day (Niesz et al., 2010; Ould-Ely et al., 2011).

**References:**


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