(U) Point Forecast for Small Energy Storage and Ultrathin Electronics

March 2010

This report was prepared by Sandia National Laboratories, Systems Assessment and Research Center, for National Security Agency. The views expressed are those of the project personnel and not necessarily those of NSA.

Sandia Systems Assessment and Research Center Document

(U) Point Forecast for Small Energy Storage and Ultrathin Electronics

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This work is sponsored by National Security Agency, Research Transformation.

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(U//~~FOUO~~) Recent advances in engineering of thin architectures for traditional electrical components have led to new applications in smart card technologies, wearable sensors, and low profile communication devices. The technologies driving this innovation are the development of thin energy storage elements and thinning of traditional silicon electronics. This point forecast covers recent advances, both within the United States and within other nations, in thinning traditional chemical energy storage systems (such as batteries and electrolytic devices), as well as efforts in small energy storage from mechanical and radioisotopic conversion systems. In the area of ultrathin semiconductors, the forecast discusses efforts to produce electronics at 50 micrometers down to 5 micrometers with high reliability by using traditional thinning methods, as well as novel processes or different choices of semiconductors, particularly organic based systems.

(U) Point Forecast for Small Energy Storage and Ultrathin Electronics

(U) Background and Forecast Introduction

(U//~~FOUO~~) The storage of energy, as opposed to the conversion of energy from one form to another (which is what harvesting systems do), requires the capability to change the state of a storage element to allow the energy to be withdrawn from the system. At the most fundamental level, the form of the energy storage is simply the potential energy of the storage system, and any system that has potential energy is an energy storage system. Practical energy storage systems require the ability to take the stored potential energy and do useful work with it, and this additional requirement starts to place restrictions on how the energy storage system is designed. Typically, the potential energy density of the system is of paramount importance, especially when one is considering small energy storage systems; but only slightly less important is the rate of conversion of the energy from stored energy into useful work. A storage system that can store tens of thousands of joules of energy is not useful if the energy only comes out in nanowatts; similarly, an energy system that can supply watts is generally of little use if it only stores a microjoule.

(U//~~FOUO~~) With this in mind, there are several main areas of relatively practical energy storage with appropriate conversion rates. By far, the most available and practical system is the chemical storage system—what is commonly called a battery. In these systems, the chemical potential of a reaction is converted electrochemically into useful work by separating an oxidation reaction, which generates electrons from a reduction reaction that consumes the electrons. If an electrical circuit is placed between these two half reactions and the electronic pathway is forced through the circuit, stored energy is extracted into useful electrical work. Batteries have become ubiquitous within our society because of their relatively high energy density and ability to source significant rates of energy release. However, most of the highly energetic chemistries that are used in batteries are intolerant to moisture and oxygen, and are toxic or corrosive, and must be packaged to protect both user and chemistry. As the battery dimensions are reduced, the package thicknesses do not scale linearly with the scaling of the system size, and so the volume of active material, as a percentage of the whole volume, decreases as size decreases. Most very small batteries boast a volumetric energy density that is only a fraction of what the chemistry would otherwise deliver, mostly due to the packaging issues. New methodologies for battery manufacture are beginning to come to the fore to overcome this issue, and will be discussed both in the battery architectures section, as well as the battery chemistries section.

(U//~~FOUO~~) The other methods of storing energy discussed in this study have energy densities that are very low relative to batteries, either due to fundamental limitations of the storage method, or due to immaturity of the technology itself. Electrolytic capacitors are a form of electrochemical storage—like a battery—but lack the battery's capability to store energy in the form of chemical potential energy, relying instead on storing energy only in an electric field between ionic concentration gradients. They can release this energy very quickly, however, and so can generate significant power, albeit for a shorter time than an equivalently sized battery. Mechanical energy storage, typified by microelectromechanical systems (MEMS), can also store small (millijoule) levels of energy in forms, such as wound springs and turning flywheels, but this energy can also be released quickly, leading to high instantaneous rate of discharge for such elements. They are typically not reversible, however (with flywheels being the exception), so that when a mechanical element is "discharged" or released, it requires external intervention to reset the mechanical elements to allow for another discharge event to occur. Although the field of research in this area is rather small (and therefore not very well focused), there are still a few efforts to produce mechanical power (typically then converted to electrical work through piezoelectric transduction or electromagnetic alternators). Finally, although not truly "storage" elements, radioisotopic energy sources

are often considered storage elements, although they consist of an irreversible radioisotopic energy source coupled to an energy conversion (harvesting) system. The reason they are considered "storage" elements is due to the lifetime of elements employing a radioisotopic element being comparatively long, and therefore acting similarly to a rechargeable element that can be fielded for a very long period of time. The field of radioisotopic energy concepts is built upon the work to make small scale thermoelectric power sources (mostly for medical applications), and expands into developments of direct conversion devices that take the emitted charged particles and convert them into electrical signals.

(U//~~FOUO~~) The final part of this study does not involve energy, but application. For most small power sources, the energy density and the rate of discharge are sufficient to power some form of electronics. Although electrical circuits are the thickness of the substrate into which they are fabricated, with current dimensions being in the 0.5–1 millimeter (mm) range, there is growing interest in thinning these active circuits to very thin (and therefore flexible) geometries, on the order of 5–50 micrometers (μm). At these geometries, however, reliability and functionality are significant concerns, especially with regards to heat sinking of the circuit, and of defects generated during thinning propagating into the functional regions of the device, in particular the gate regions. Wet chemical methods have been developed to deal with surface damage, at least in part, that allows for thinning into the 5–30 μm range. This area is still heavily US-dominated, although international efforts in the area are scaling up, and the ubiquity of such ultrathin microelectronics is increasing and will be reviewed in the final section.

(U) Methods of Data Mining Used in the Forecast

(U//~~FOUO~~) The methodology in accomplishing this assessment consists of three main elements—acquisition of the data, map development and characteristics, and the analytical session. The data used to conduct this assessment was derived from Web of Science, Inspec, and ISI Proceedings. Web of Science was used in order to cover Technology Readiness Levels (TRL) one to three. Inspec was used in order to cover the higher Technology Readiness Levels four and higher. ISI Proceedings were important to include since they cover conference proceedings, which tend to be timelier than traditional journal papers.

(U//~~FOUO~~) The previously mentioned databases where queried by using a set of terms provided by the subject matter expert. Each technology within Energy Harvesting was isolated and queried and analyzed separately. In most cases, an iterative approach to query enhancement was used in order to identify secondary enabling technologies such as materials.

(U//~~FOUO~~) The second element of the assessment consisted of constructing a "landscape" visualization that enabled effective analysis of thousands of documents at a time (figure 1). The "landscape" visualization is an incredibly dynamic analytical environment that resembles the interactivity of Google Earth. The visualization allows the user to get a high-level view of a corpus of data, and within seconds the user can zoom down to an individual document. As the user zooms down, clusters of related documents automatically and repeatedly break up into smaller sub-clusters. As the user zooms in, each cluster is automatically label by using the most prominent terms within the current cluster. In regards to cluster size, the density of documents is portrayed by the clusters height and width. For example, documents within a cluster that are very similar will tend to create a very tall and thin peak, as opposed to a less similar set of documents, which will result in a very wide but shallow hill.

(U//~~FOUO~~) In order to develop the landscape visualization, the similarity value between each of the documents needed to be calculated. This was accomplished by running a Latent Semantic Analysis (LSA) algorithm across each document's Title and Abstract fields. As a result, each document is given a similarity value comparing it to every document in the corpus. The LSA algorithm is completely unassisted and does not require any sort of ontology or taxonomy. As a result, there is no bias injected into the process of creating the clusters of similar documents.

(U//~~FOUO~~) The third element of the assessment consisted of a three to four hour session with each of the subject matter experts.

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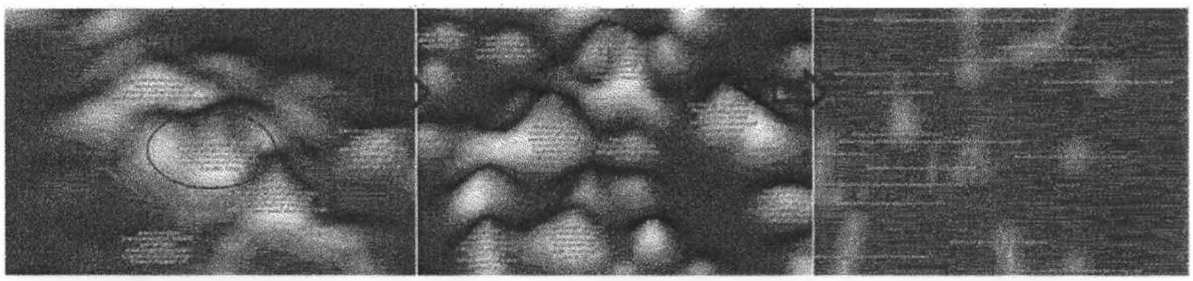

Figure 1. **(U//~~FOUO~~) Zooming from a Global View to Each Document**

(U//~~FOUO~~) The session comprised of interactively navigating through the landscape visualization environment with the subject matter experts to identify interesting patterns, trends, and relationships. When an interesting element was found, it was captured using mindmapping software, enabling the session to be focused, organized, and effective by tracing what has been assessed and found almost instantly. A handful of sessions chose to start out with the mindmap in order to capture the components of a technology before assessing the landscape visualization. At the conclusion of the session, a mindmap of the session (figure 2) was sent to the subject matter experts in order to provide them with material to conduct deeper analysis of the interesting elements that were found.

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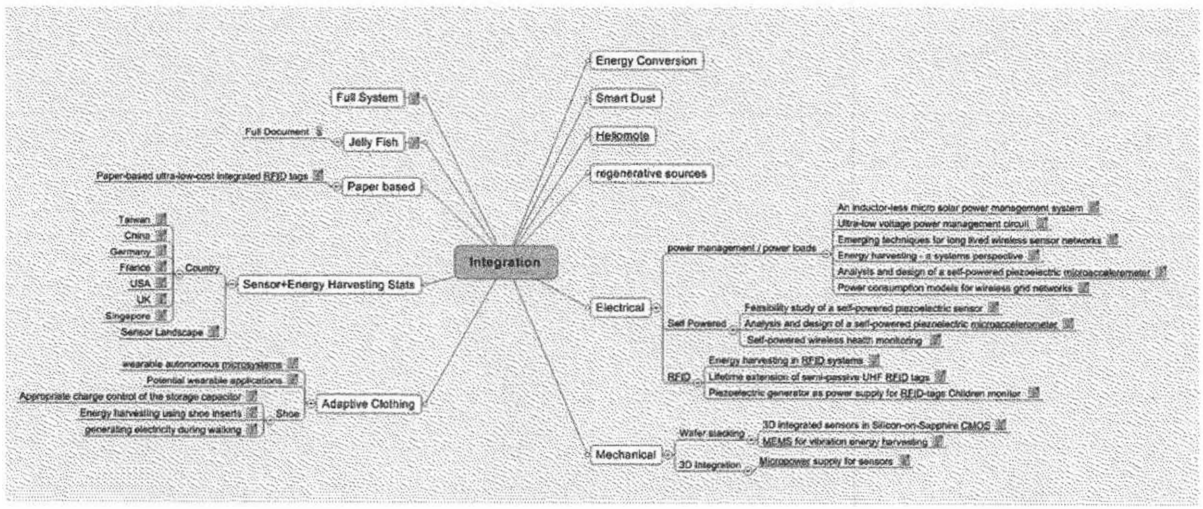

Figure 2. **(U//~~FOUO~~) Example of Mindmap Capturing Interesting Elements from a Session**

(U) Ultrathin and Printable Batteries

(U) Introduction to Batteries

(U//~~FOUO~~) Low profile power sources are in development for in-package energy storage, with potential for significant energy density and power density to power active devices. Several approaches to ultrathin (sub-500-micron) and printable batteries are in current development worldwide. In particular, groups at Nippon Electric Company (NEC), DuPont Teijin, University of California at Berkeley, Massachusetts Institute of Technology, Sandia, and Thin Battery Technology (TBT) are among those active in the field of thin, flexible, liquid phase battery development. Battery sizes are currently generally 5–50 mm in lateral dimension and from 100–2,000 microns thick. Due to packaging consuming greater fractions of battery volume, a decrease in capacity from 200 watts per hour to 36 watts per hour is observed on decreasing thickness from 450 microns to 100 microns, scaling roughly inversely with thickness. Such batteries provide roughly 1–24 milliamperes per hour of capacity; for a 1-milliwatt, these power sources provide only 3–72 hours of operation. The interest in printed batteries stems from the ability to print conformal, flexible batteries with less inert packaging volume, application-tailored power density and energy density, and potentially three times higher energy density than currently available commercial-off-the-shelf (COTS) packaged batteries.

(U//~~FOUO~~) Integrated thin-film battery sources are increasingly becoming available based on either thin film solid electrolyte technology (sputtered micron-thickness films and lithium phosphorus oxynitride-LiPON- electolytes) or tape-cast or printed liquid electrolyte technology (100–500 micron thickness films with liquid electrolytes). These COTS batteries, available as commercial lithium and alkaline Zn-MnO_2 (zinc-manganese oxide) cells, may provide the needed power for several applications. The ability to conformally print batteries of desired discharge characteristics is under current development at several universities and companies. Developing this capability requires expertise in battery development, battery evaluation and validation, battery integration, and end-user mission space determination.

(U//~~FOUO~~) Several thin cell liquid electrolyte systems are under current investigation including lithium cobaltate ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMnO_2$), lithium iron oxide ($LiFe_2O_3$), lithium halides ($LiFeF_3$, LiI, LiF), manganese oxide (MnO_2) alkaline batteries, and several alternative battery chemistries. These chemistries are fabricated as button cells, pouch cells, and direct written batteries.

(U) Analysis Methods for Batteries

(U//~~FOUO~~) For simplicity of analysis, thin batteries are divided into two categories—printed batteries and sputtered batteries (for example, Front Edge Technologies or IPS (Infinite Power Solutions) thin cells). Sputtered batteries are often on rigid substrates (silicon, mica, alumina) and processed at high temperatures (greater than 500 °C); they may be difficult to integrate compared to printed batteries on paper or flexible polymer substrates, but potentially very thin (fewer than 100 microns on thin silicon or mica, for instance).

(U) Printed Liquid Electrolyte Batteries

(U//~~FOUO~~) A very significant effort in printable lithium and other printable batteries based on liquid electrolytes is being conducted in the Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials under Prof. Z. Jiang. Among the capabilities developed at this group are high discharge rate printed batteries with high initial discharge capacity, 1.2-volt silicon dioxide/lithium (SnO_2/Li) batteries, with 812.7 milliampere-hour per gram (mAh/g) capacity at 33 milliampere per square centimeter discharge current. They also claim a printed, 1.2-micron-thick, 3.4-volt $LiCoO_2$ cathode battery; assembled Li/$LiCoO_2$ cells displaying 120 mAh/g capacity, and discharge current of 180 microampre per

square centimeter ($\mu A/cm^2$) (at this rate, the battery can be fully discharged in 12 minutes, a 5C[a] rate). Further work from this group uses more esoteric battery materials, such as a printed 1–2 volt lithium-ion battery using 1.7~1.8 µm lithium titanate ($Li_4Ti_5O_{12}$) anode film with 174 mAh/g capacity, and 10.4 $\mu A/cm^2$ discharge current, and a printed MnO_2 nanoparticle ink on gold substrates with a capacity of 270 mAh/g at a current density of 4.01 ampere per gram (~1.6 mA/cm^2).

(U//~~FOUO~~) An Israeli group at the Technion Laboratories[b] and elsewhere are working on aspects of microbatteries and 3-D microbatteries based on MEMS and thin film integration. A 2–3.5 milliampere-hour per square centimeter (mAh/cm^2) thin-film battery was fabricated on a corrugated, microfabricated substrate to provide high surface area. The design was $LiMnO_2$ cathode, lithiated graphite anode, and a polymeric electrolyte. This microfabricated thin-film battery with a 1-micron-thick cathode was able to discharge at 2C[a] rates.

(U//~~FOUO~~) Significant work on liquid electrolyte batteries, presumably for consumer applications, is being developed by several groups (Samsung, Universityersities) in South Korea, primarily focused on lithium vs. screen printed, 6–10-micron-thick $LiCoO_2$ or lithium manganate ($LiMn_2O_4$) cathodes. It is proposed this method could be applied to solid state batteries, but the method requires high-temperature processing (600 °C) incompatible with flexible electronics.

(U//~~FOUO~~) The Fraunhofer Institute (Chemnitz) in Germany has reported screen printable battery chemistries for 1.5-volt operation, such as Zn-MnO_2 batteries, and Sandia has demonstrated printed $LiFePO_4$ versus lithium titanate ($Li_4Ti_5O_{12}$), which is of interest, although multiple cells would be needed for 3-volt logic operation. Printable batteries are of increasing interest and will be increasingly commercially available, with thicknesses at the 400-µm level up to several millimeters. Packaging thicknesses are often a dominant limitation of these cells, typically contributing ~200 microns of thickness. With careful choice of packaging, liquid electrolyte cells in the 200–400-µm range may ultimately be developed.

(U//~~FOUO~~) Manufacturing of a variety of relatively thin (400 µm to 2 mm) liquid electrolyte batteries such as Powerstream™ is conducted in China for a variety of US customers, including US law enforcement, in formats from 1 cm^2 to 8.5 inches × 11 inches. These are typically produced by thick-film processing (screen printing or doctor blade processing).

(U) Sputtered and Solid Electrolyte Thin-Film Batteries

(U//~~FOUO~~) There is little reported work on sputtered thin film batteries from China or Russia; the majority of reported work is from the United States, from such locations as Eveready Battery Company, Oak Ridge National Laboratories (ORNL), MIT, and UC Berkeley.

(U//~~FOUO~~) The thin-film sputtered battery originally demonstrated at ORNL and now produced at Front Edge Technologies and Infinite Power Solutions/IPS is of interest for a very thin form factor (100–300 micron), but is somewhat limited in energy (0.1-1 mAh/cm^2) capacity compared to the 450–2,000-micron-thick liquid electrolyte cells above (2–5 mAh/cm^2; for example, Solicore™ and Powerstream™).

(U//~~FOUO~~) In the United States, ORNL and Dudney et al reported operation of solid state batteries using a Li/LiPON/$LiCoO_2$ topology with 40-nanometer (nm) to 4-µm $LiCoO_2$ cathode thickness. This technology has been transferred to IPS and Front Edge Technologies for microfabricated batteries. These cells are of interest, but difficult to use for large current draw applications due to internal resistance and limited discharge rates (1C rates). NASA's Jet Propulsion Laboratory (JPL) has publicly reported processing methods for fabrication of very small batteries (50 µm × 50 µm) with 3.9-volt operation, but

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[a] (U//~~FOUO~~) 1C indicates a charge rate equal to the capacity of the specified battery in a period of one hour

[b] (U//~~FOUO~~) Golodnitsky D.; Strauss E.; Freedman K.; Peled E.; Burstein L.; Gladkich A.; Nathan M.; Yufit V. Ripenbein T.; Shechtman I.; Menkin S.

very small energy densities (10 microampere-hour per square centimeter) based on lithium/lithium phosphorus oxynitride/ lithium manganese nitrate (Li/LiPON/Li_3MnNiO_4). JPL has also developed an alternate solid state electrolyte, lithium phosphate/lithium silicate (Li_3PO_4/Li_4SiO_4). MIT reported sub-50-micron batteries using lithium/block copolymer/200-nm vanadium oxide (VO_2) architecture, with 395 mAh/g capacity (neglecting packaging). MIT also reported use of very thin 4–40-nm silica (SiO_2) as a solid state separator to fabricate 2.2-volt $LiCoO_2/SiO_2$/poly-silicon batteries, an unusual approach. Eveready reported a thin-film battery technology based on a sputtered titanium sulfide(TiS_2) cathode, sputtered glassy electrolyte, evaporated lithium iodide (LiI) layer, and a lithium anode.

(U//~~FOUO~~) Because of the thin profile of sputtered batteries, close attention to sputtered or thin-film battery development is likely warranted. The majority of work to date has been US or German, but international efforts are increasing, particularly in China. In place of a polymer separator and liquid electrolyte, a lithium conducting film, such as lithium phosphate ($LiPO_4$), LiPON, or lithium-lanthanum tantalate ($Li_xLa_{1-3x}TaO_3$ is used as a solid state electrolyte. This film may be deposited by vapor phase methods, such as sputtering, evaporation, or other vacuum thin-film deposition methods. Recently, US workers have demonstrated non-vacuum integration of these films on copper electrodes by solution deposition and processing in a hydrogen-containing atmosphere, which may ultimately enable printed solid state electrolytes—but this is a challenging approach.

(U//~~FOUO~~) Worldwide efforts in solid-state thin-film lithium batteries (TFLB) and solid state lithium electrolyte fabrication approaches are increasing, and the following sections discuss each country's efforts in this area.

(U) Foreign Work in Batteries

(U) China

(U//~~FOUO~~) The Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials has a significant effort at sputtered thin-film batteries, such as an all-solid-state cell based on Li/LiPON/$CuWO_4$ topology, which displayed 145 µAh/cm^2-µm. Similar cells based on Li/LiPON/$Ag_{0.5}V_2O_5$ were reported to display 3-volt discharge, and up to 550 cycles of operation at a discharge capacity of 62 µAh/cm^2-µm. Alternate solid state electrolytes have been developed at the same Shanghai laboratory:

> "$LixMn_2O_4$ and $Li_xMn_2O_4$-0.5 ZrO_2 thin films have been fabricated by radio frequency sputtering deposition combined with conventional annealing, and the other three vacuum chambers for deposition of current collectors, cathode and solid electrolyte by magnetron sputtering, respectively." [a]

> "This equipment has been used to sequentially deposited Au current collector, TiO_2 cathode, LiPON (lithium phosphorus oxynitride) solid electrolyte and metallic Li anode thin films, and to prepare a TFLB with a structural configuration of Li/LiPON/TiO_2/Au via an in-situ process without breaking vacuum." [b]

(U//~~FOUO~~) A group at Fudan University in Shanghai has developed chromium nitride (CrN) cathodes for thin film lithium battery applications, as well as sputtered nickel and zirconia containing lithium cobalt oxide ($LiCo_{0.8}(Ni,Zr)_{0.2}O_2$)cathode films.

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[a] (U//~~FOUO~~) Li C.-L.; Fu Z.-W. "Solid-state Rechargeable Thin Film Lithium Batteries with LixMn2O4 and LixMn2O4-0.5ZrO2 Cathodes". Electrochimica Acta (2007).

[b] (U//~~FOUO~~) Liu W.-Y.; Fu Z.-W.; Qin Q.-Z. "A sequential thin-film deposition equipment for in-situ fabricating all-solid-state thin film lithium batteries". This Solid Films (2007).

(U//~~FOUO~~) A group at the University of Science and Technology in Anhui, Hefei Province, is developing solid state electrolytes for solid state thin film batteries (similar to IPS and Front Edge Technologies products) in the group of C.H. Chen.

(U//~~FOUO~~) This group also demonstrated thin solid state batteries with solid state electrolytes based on a copy of a Bellcore technology (Li_3PO_4). Solid state thin film electrolytes were composed of a composite of Li_3PO_4 and SiO_2 nanoparticles, dibutylphthalate (DBP) and a poly(vinyldiene fluoride) PVDF matrix.

(U//~~FOUO~~) The Beijing Institute for Technology has demonstrated both sputtering of anode materials for thin film batteries, as well as development of alternate solid electrolytes. Li-Al-Ti-P-O thin-film electrolytes were prepared by magnetron sputtering, which was not reported in literature. The ionic conductivity of the thin-film electrolyte was 10^{-6} Siemens per centimeter (S/cm) at 25 °C, and the electrochemical window of this electrolyte was about 3.5 volts. This kind of electrolyte with good physical chemistry properties is a candidate material for solid state thin-film lithium batteries with improved performance over the currently existing (LiPON) chemistries.

(U//~~FOUO~~) Research efforts on sputtered batteries are also present at Zhejiang University in Hangzhou, Xiamen University, and University of Science and Technology in Beijing. The efforts at the two Shanghai Institutes (Wuhan University and Shanghai Key Laboratory for Molecular Catalysts and Innovative Materials) appear the most mature, however, and most similar to the ORNL/IPS and JPL thin-film battery inventions. It should be concluded that there is a manufacturing capacity in Shanghai for microfabricated thin film batteries of very small thickness (less than 50 microns), though with limited energy density and power capacity (current draw) due to the use of low conductivity LiPON-based solid electrolytes. In addition, the work at University of Science and Technology in Anhui suggests development of flexible solid state batteries with potentially low profiles (less than 100 microns).

(U) Taiwan

(U//~~FOUO~~) National Tsing Hua University and Academica Sinica reported sputter deposition of 1.55-volt thin-film lithium batteries based on lithium/lithium titanate ($Li/Li_4Ti_5O_{12}$) cells, with 65 mAh/cm^2-µm capacity. Also, Feng Chia University reported sputter deposition of $LiCoO_2$ battery cathodes, applicable to generation of 3.5-volt lithium thin-film batteries.

(U) France

(U//~~FOUO~~) HEF Research and Development in Andrezieux-Boutheon report fabrication of batteries for smart card applications in the range of 100–400 microns thickness. Also, Souquet and Duclot at LEPMI, UMR CNRS in Saint Martin d'Heres report 1–3-mm-thick hybrid plastic electrolyte lithium cells with a few mAh/cm^2 capacity. CEA-Grenoble reported in 2008 development of an above-IC microbattery in which "the components of the battery including the current collector, cathode, anode, and electrolyte were all deposited on a silicon wafer at room temperature using standard sputtering and evaporation techniques." [a]

(U) Japan

(U//~~FOUO~~) Geomatec and Taiyo Koko are two companies active in thin film lithium battery research and development, reporting alternate cathode materials for sputtered thin film cells. Short term, 0.1-mAh cells of a few microns thickness are listed as commercially available by Geomatec; the cells appear to have been jointly developed with Iwate University.

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[a] (U//~~FOUO~~) Roche S.; Navone C.; Sanchette F.; Gaillard F.; Laurent J.; Rouault H.; Marsacq D.; Salot R.; Pereira-Ramos J.-P., "Above IC Microbattery". Meeting Abstracts - 205th Meeting of The Electrochemical Society, MA 2004 01, San Antonio, TX, USA (2004)

(U) Summary of Batteries and Future Trends

(U//~~FOUO~~) In general, battery trends are driven by multiple independent market forces, each trying to locally optimize. The markets can generally be broken up into batteries for portable applications, batteries for grid power stabilization, and batteries for transportation. Thin-film batteries fall into the third category, and consumer electronics will lead the way for this community for the foreseeable future. Within this, significant efforts both in liquid electrolyte and solid electrolyte battery architectures are being made. Thicknesses of 400 mm are already commercially available, and it is likely that these will shrink to around 250 mm or so with no loss in energy density, driven mostly by the need for flexibility in battery casings to accommodate flexible displays and computer interfaces. Biomedical implants may also be a driver for this community, although energy densities needed for biological systems may force this community back into a densely packaged 3-D architecture, rather than remaining flat. It is clear from the work here that printed batteries will become commonplace, likely within the next five years, but they will primarily be low energy density, and disposable (environmentally friendly) single use systems. Rechargeable batteries do not have the driver to thin that the disposable community is driving, and may lag the primary battery community simply because of the lack of drive to thin. However, energy density gains, made mostly through packaging innovations, will become a significant driver for portable rechargeable electronics. It is likely that China and Japan will lead this effort, with significant assistance and input from the European community.

(U) Introduction to Battery Materials

(U//~~FOUO~~) While the United States led all battery efforts in the past two decades, in the last five years a large increase in battery research has occurred for every country, with a dramatic upturn noted for China, Japan, and Korea. Just recently, China has overtaken the research efforts reported by the United States. The graph in figure 3 shows the number of papers being published by these four countries. Interestingly, two noticeable "bump-ups" were noted in the number of publications for the community with a substantial increase in 2004 and then again in 2008. From these papers, it is clear that lithium-ion batteries have come to the forefront of research efforts. Lithium-ion batteries were commercialized in the early 1990s with intensive efforts for materials development to increase the power and decrease the weight of the batteries. There are numerous efforts in developing materials for a number of battery types as well. The problems that need to be overcome include higher capacities, higher voltages, overheating and failure, and of increasing interest "green" materials. These materials and the personnel involved in the development of the three components of a battery (cathode, electrolyte, and anode) are discussed individually below. The synthesis routes are not discussed in that these are numerous and typically optimized for the individual material being investigated.

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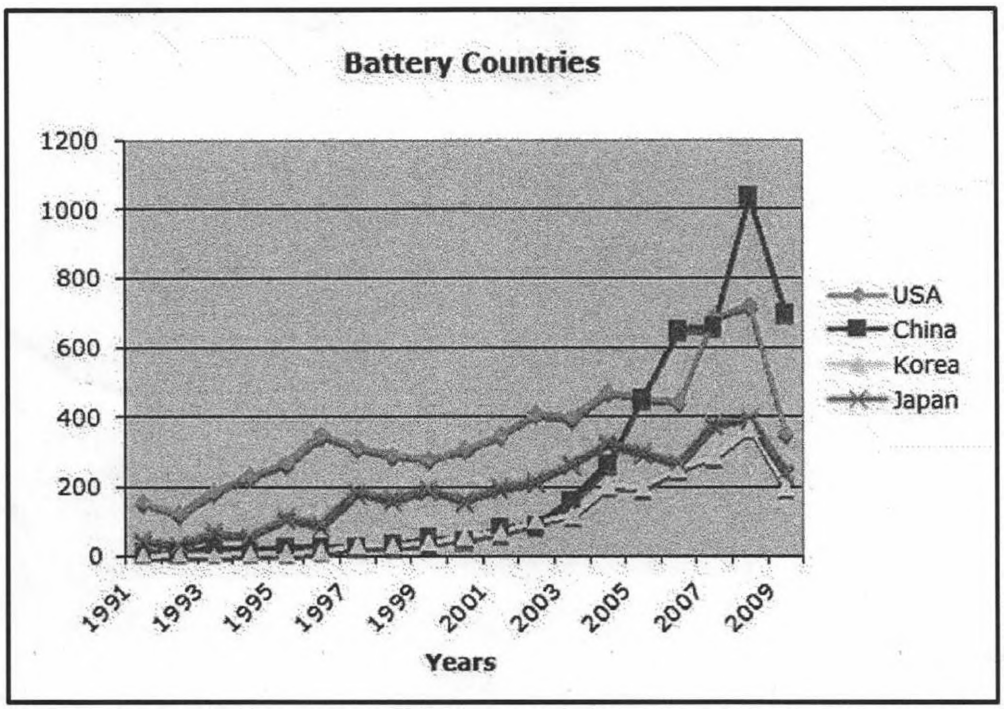

Figure 3. (U//~~FOUO~~) Number of Publications by Year from the Leading Four Countries in Thin Film and Printable Batteries

(U) Anode Battery Materials

(U//~~FOUO~~) The leading countries in the material development of anode materials are China (3,500: approximate number of authors published in the past 10 years), Japan (3,200), USA (2,300), and Korea (1,600), which account for more than 80 percent of the research efforts. Removal of the United States from consideration reduces the work only 20 percent with China presenting the majority of research focused on lithium-ion batteries. The work on the synthesis of these materials has steadily grown over the past five years, with 2007 being an extremely high level of publication in this area.

(U//~~FOUO~~) In looking at the non-lithium battery work, three researchers stand out—S. Licht, J. Y. Lee, and F. Wu. The chemist Stuart Licht started in Israel working on aluminum batteries, switched to iron-based batteries. He moved to the University of Massachusetts and now to National Science Foundation (NSF). Recently his work has focused on metal boride (vanadium, iron) that he indicates are a substantial improvement over lithium- based batteries. Jai-Young Lee of the Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology has also been involved in non-lithium-based materials for battery applications. He published routinely from 1996 to 2006 with his fellow countrymen. His work has focused on cobalt-based anodes with typical transition metal doping schemes. In addition, he has dabbled in hydrogen storage. His latest papers were investigating silicon-based composite materials. Finally, F. Wu from the Beijing Institute of Technology and his coworkers in China have been working on cobalt effects on nickel-metal hydride materials and lately, has also started looking at cobalt-boron alloys. Combined the non-lithium work is limited but appears focused on the borohydrides and cobalt metals.

(U//~~FOUO~~) Organic and inorganic materials have been used to generate lithium ion battery anodes with Japan, China, United States, and Korea leading the way, the effort of which has been relatively steady for the past five years.

(U//~~FOUO~~) Typically for organic these materials have focused on graphite with Y. P. Wu (now moved to China) as the leader in the field working for R. Holze of Germany. Additionally, K. Zaghib of Canada is also heavily involved in developing graphitic based materials whose surfaces can be modified by mild oxidation, deposition of metals and metal oxides, coating with polymers and other kinds of carbons yield useful anodic materials. Wu is currently working on nitrogen-doped polymeric (PAN) carbon materials, while Holze is working on other polymeric systems (PANI and POT) and Zaghib is exploring graphite anodes with $LiFePO_4$ cathodes. Additional research efforts by M. Endo (Shinsu from MIT) and Canada's J. R. Dahn have focused on similar efforts.

(U//~~FOUO~~) The vast majority of anodes for lithium-ion batteries come from transition metal oxides, which range from magnesium (O. Hasvold, and D. Aurbach), aluminum (S. Licht and M. Morita), silicon (T. Takamura and M. Yoshio), titanium (Z.W. Zhao), vanadium (D.R. Sadoway and A.M. Mayes), manganese (N. Kumagai and M. Wakihara), iron (J. Shim and S. Licht), cobalt (J. Xie and H.K. Liu), nickel (J.Y. Lee, and H.K. Liu), copper (C. Wan), zinc (S. Licht and C.W. Lee), silver (Y.P. Wu and J. Yin), tin (H.K. Liu and Y.P. Wu), lanthanides (S. Garcia-Martin), and lead (J. Morales and P.N. Kumta). Each of these metal oxides has hit a high mark in the past 10 years concerning reports published. Consistently lower in the number of reports are lead, vanadium, and manganese with less than 10 reports noted for their peak years. The majority of metals have 20 –40 papers reported at their height, but the most reported metals involve iron, silicon, and tin, which have all peaked in the last four years. Tin oxide has an order of magnitude higher number of publication than the rest for anode materials, peaking in 2007. H. K. Liu (Wollongong University, Australia) has been the most published researcher with a focus on pure and doped tin oxide (SnO/SnO) porous nanomaterials on a variety of substrates. Y. P. Wu and co-workers at Tsinghua University in Beijing are also investigating carbon matrices with nano-SnO_x materials. Additionally, there have been recent (2009) efforts to employ silicon and germanium oxide (SiO_x and GeO_x) nanowires as anode materials by Y. Cui at Stanford.

(U) Cathode Battery Materials

(U//~~FOUO~~) Substantial efforts have also been undertaken on the production of new cathode materials. The main countries involved in the development of battery cathode materials are China (4,700), Japan (3,300), United States (2,900), South Korea (2,000) followed by a substantial drop-off to France, India, and Germany. Again, the majority of work has focused on lithium-ion batteries; however, there is some work on non-lithium species that should be mentioned.

(U//~~FOUO~~) The non-lithium battery cathode materials have focused on the standard lead, zinc, and nickel batteries. The lead cathode materials effort has been fairly consistent over the past 10 years with only a handful of researchers focused on this system. The lead-acid battery effort is led by H. Karami and M. Shansipur of Iran's Payame Noor University in Abhar, but China, the United States, and Korea have small efforts as well. Additionally, more research has been undertaken on zinc/air batteries with Licht (vide infra) leads the charge followed by India's R. Renuka from Central Electrochemical Research Institute in Madras; however, China leads the effort in this area as well. Nickel cathode materials appear to be of interest but these typically are mixed with other cations and not the focus the cathode material.

(U//~~FOUO~~) The majority of work in the cathode field appears to focus on the lithium ion batteries. The materials of interest appear to be the layered oxide materials consisting of lithium M oxide (LiMOx) where M = manganese, nickel, cobalt. One of the most studied lithium ion battery cathode materials is the layered oxide $LiMnO_x$, since it yields a relatively high theoretical capacity coupled with its "dirt cheap" cost. The Japanese (3,000) and the Chinese (4,200) lead the research efforts on this work followed by the United States (2,500) and Korea (1,800). Of these researchers, Japan's Masaki Yoshio of Saga University

has published extensively on melt impregnation methods for the preparation of LiMnOx materials for both 3- and 4-volt batteries. Y. -K. Sun of Hanyang University in South Korea has done work on manganese cathodes along with other metal cation dopants (that is, aluminum, nickel, cobalt). The third researcher is Manthiram from the University of Texas, who focuses on new routes and doping of manganese oxide for cathode materials. The layered oxide $LiNiO_2$ has been investigated mainly by US researchers Amine (ORNL), McBreen (BNL), and Manthiram (UT). The major researcher from Japan is N. Kumagai from Iwate University, who has focused on a variety of transition metal oxides. China has a large effort with C.-Y Jiang and C. Wan of Beijing's Tsinghua University having done some work on this material, but they have mainly focused on mixing with other cations (vide supra). The most promising and commercially viable cathode material for lithium-ion batteries is $LiCoO_2$. This has been extensive studied by the China, United States, Japan, Korea, and Taiwan. Y. Yang of Xiamen University, and J. Li and C. Wan of China's Tsinghua University in Beijing are the leading researchers, but this cation appears to be mixed with the other cations. The mixtures of cations dominate the layered oxide materials that are used for cathodes. The cations typically are variable molar ratios of manganese, cobalt, nickel and pretty much the rest of the periodic table. There does not appear to be a consensus on the most useful combination of cations.

(U//~~FOUO~~) Recently, $LiFePO_4$ has come to the forefront of cathode materials, due to the high capacity, relative green aspect, and low cost for production. Canada's K. Zaghib of the Institut de Recherché Hydro in Quebec spearheads these research efforts, optimizing purity and doping with carbon sources to improve the capacity. A majority of this work has been done with F. Grendon and C. M. Julien of the Institute Nanosci in Paris, focusing on the synthesis, characterization, and some testing of $LiFePO_4$ glasses. China's efforts are focused on the synthesis by Z. X. Wang of Cent South University of Technology, H. Xie, and J. Xie. Additionally, US researchers E. J. Cairnes from Lawrence Berkeley Labs and J. Prakash of Argonne Labs have done some leading edge work on this material.

(U) New Electrolytes for Batteries

(U//~~FOUO~~) The electrolyte portion of the battery is probably the most important and the most difficult in terms of properties to achieve. This work is broken down into organic, inorganic, solids, and liquids. The countries most active in this area include China, which has made nearly double the effort than Japan, the next country. Japan is followed quickly by United States, Korea, and India.

(U//~~FOUO~~) Three subsets of the organic electrolytes were investigated—non-lithium, lithium, and polymer. Interestingly, non-lithium is one area in which China is not the lead. Both Japan and the United States have more research efforts ongoing, with Japan focusing more than double the effort of the United States. The leading researcher appears to be Austria's Martin Winter of Graz University of Technology, who is focusing on the redox chemistry of organic species on graphite. Also studying electrolytes is J. Schoonman from Netherland's St. University Utrecht, who is focused on fluoride conducting electrolytes. Japan's J. –I. Yamaki from Kyushu University is working on the theory of conductive fibers or particles.

(U//~~FOUO~~) M. Winter leads the way in lithium species on aqueous and non-aqueous electrolytes with some emphasis on sulfites (dimethyl and diethyl) as co-solvent for ethylene carbonate based electrolytes with graphite anodes. Polymers are developing as led by Italy's B. Scrosati at Rome University, with an emphasis of polyethylene oxide; however, it does appear that he writes a great deal of reviews.

(U//~~FOUO~~) Another means to think about electrolytes are as solids or liquids. For solid electrolytes that are employed in lithium-ion batteries, Japan is by far the leader followed by the United States and China. Scrosati again spearheads the research efforts, but Japan's Tatsumisago of University Osaka Prefecture follows closely with an emphasis on lithium-ion conducting glasses and glass-ceramics. Additionally, Golodnitsky from Tel Aviv University in Israel is working on polyethelne oxide polymer electrolyte. Both of the last two authors work with Tel Aviv University's E. Peled, who appears to be an electrochemist. Non-lithium systems are also of interest with the same authors being the leaders. A search

of ionic electrolytes also indicates that Scrosati is the main publisher, followed by L. Chen at Argonne National Laboratory in the United States. Another new name that appears often is Appetcchi who works with Scrosati and Passerini from Rome University. Considerable research has also focused on lithium bis-oxalato borate ($LiB(C_2O_4)_2$ or, LiBOB), with a peak in papers published in 2006 and holding steady since then. The main researchers are in the United States, led by T.R. Jow, who published mainly with K. Xu and S. S. Zhang from Army Research Labs, Adelphi, MD.

(U) Future Trends in Battery Materials

(U//~~FOUO~~) China, Japan, and Korea have put forth a major effort on secondary lithium ion batteries. The countries working on new battery materials are China (C. Wan, C. Jiang, L. Chen), Japan (M. Yoshio, K. Kanamura, J. I. Yamaki), and Korea (Y. K. Sun, H. S. Kim, S. I. Moon). Interestingly, their emphases are different (table 1):

- China
  - Cathode > anode
  - Electrolyte not in the top 20 keywords
- Japan
  - Electrolyte > cathode > anodes
- Korea
  - Cathode > anodes
  - No electrolyte

Table 1. (U//~~FOUO~~) Researchers by Battery Component

	China	Japan	Korea
Anode	Y. P. Wu and L. Chen, Chin. Acad. Sci.	T. Takamura, Rikyyo M. Endo, Shinsu/MIT	J. Y. Lee, Korea Adv. Inst. Scit Eng. H. –J. Sohn Ieng. Consv. Stor.
Cathode	J. Li, Harbin	M. Yoshio Saga University	Y. –K. Su, Hangyang University*
Electrolyte	L. Chen, Chin. Acad. Sci. C. Wan, Tsinghua	J. I. Yamaki, Kyushu Z. Ogumi, Kyoto	H. S. Kim, Sungkyuhkwan K. W. Kim, Gyeongsang National
* Also, D. Aurbach, Bar-Illan, Israel			

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(U//~~FOUO~~) A number of materials are being studied as discussed above to improve the capacity and voltages (less than 5 volts) of the batteries with increased stability. The anode materials are far ahead of the cathode and electrolytes. The cathode materials offer best opportunity for improvement—3.5 – 4.5 volts using titanium sulfidide (TiS_x), lithium metal oxide ($LiMO_x$), $LiFePO_4$, all are currently below 500 watthour per liter (Wh/L). As the lithium ion materials discussed above are being improved and displacing most all other batteries, there are efforts underway that may offer alternative routes. These efforts include sodium-sulfur and sodium-nickel chloride-based batteries, but dendritic formation needs to be overcome. Zinc air batteries are promising, but higher capacities are needed. Of future interest, bio-batteries (fueled by and for) have attracted considerable interest.

(U) Supercapacitors

(U) Introduction to Supercapacitors

(U//~~FOUO~~) Discovered by Henrich Helmholtz in the 1800s, electrochemical capacitors were first practically used in 1979 for memory backup in computers and are now manufactured by many companies. Electrochemical capacitors (EC) are also known as "super," "ultra," "pseudo," and "double-layer" capacitors. The first products were rated at two to five volts and had capacitance values measured in fractions of a farad to several farads. Today's devices range in size up to hundreds of thousands of farads at low voltage and, in some applications, system's voltages (multiple series-connected capacitors) are above 600 volts.

(U//~~FOUO~~) Double layer electrochemical capacitors differ from other types by having capacitance and energy density values several orders of magnitude larger than even the largest electrolytic-based capacitor. They are true capacitors in that energy is stored via electrostatic charges on opposing surfaces and they can withstand a large number of charge/dis charge cycles without degradation. They are also similar to batteries in many respects, including the use of liquid electrolytes, and the practice of configuring various size cells into modules to meet power, energy, and voltage requirements of a wide range of applications.

(U//~~FOUO~~) There are two types of ECs—symmetric devices and asymmetric devices. Most of the original devices were symmetric devices. More recently, most of the work is in the area of asymmetric devices. Figure 4 shows the configuration of a typical symmetric device where the electrolyte is either aqueous (H_2SO^4, NaOH) or organic (ammonium salt dissolved in an organic solvent, such as propylene carbonate or acetonitrile). These electrochemical capac itors consist of two electrodes, a separator,

electrolyte, two current collectors, and packaging. Within the electrochemical capacitor, charge is stored electrostatically, not chemically as in a battery. It has, as a dielectric, an electrolyte solvent, typically potassium hydroxide or sulfuric acid or an organic liquid, and it is actually two capacitors connected in series via the electrolyte. It is called a double-layer capacitor because of the interface region of the electrolyte.

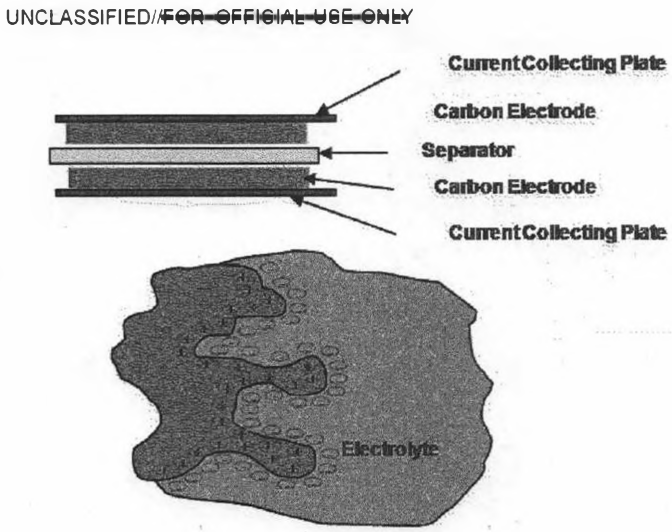

Figure 4. (U//~~FOUO~~) Typical Symmetric Device

(U//~~FOUO~~) As in any capacitor, the amount of capacitance is directly related to the surface area of the electrode. Carbon is the element almost uniquely suited for fabrication of electrodes within electrochemical capacitors. It has high electronic conductivity and is available at reasonable prices from many sources. The surface area of a carbon electrode is very large at 1,000 to 2,000 square meters per cubic centimeters. This large surface area is the reason for very high characteristic capacitance and energy density. These devices use either aqueous or non-aqueous electrolytes. Aqueous electrolytes have low resistances, but they are limited in operating range to about 0.9 volt per cell, which limits their energy output to less than the organic electrolytes that can have voltage ranges up to 2.7 volts per cell, effectively almost tripling the energy density. However, these organic electrolyte devices are limited by the facts that the dielectric constant of the organic solvent is less than that of water. The double layer thickness (plate separation) is greater because of the larger solvent molecules; the effective surface area of the electrode is somewhat diminished because the larger ion sizes cannot penetrate all pores in the electrodes. And, the ionic conductivity of the electrolyte is much less than that of aqueous electrolytes, particularly at low temperatures.

(U//~~FOUO~~) Asymmetric capacitors are comprised of two capacitors in series, one being an electrostatic capacitor and the other a faradic pseudo capacitor. The electrostatic capacitor is exactly like those used in the symmetric type. It consists of a high surface area electrode with double layer charge storage. The faradic pseudo capacitor electrode relies on an electron charge transfer reaction at the electrode electrolyte interface to store energy. This is very similar to an electrode in a rechargeable battery In this design the capacity of the faradic pseudo capacitor electrode is typically many times greater than the capacitance of the double layer charge storage electrode. Thus the depth of discharge of the faradic pseudo capacitor electrode is very small during operation, allowing higher cycle life. Again two types of electrolytes can be used—aqueous or organic. Most current devices use the same electrolytes as the symmetric devices.

(U//~~FOUO~~) The materials used for the pseudo most often are metals, including lead and nickel. For inorganic electrolytes in development, the hope is that an asymmetric device provides the opportunity for the faradic pseudo capacitive charge storage with the higher operating voltage afforded by the organic electrolyte. For example, the design could mate an electrostatic electrode with a faradic pseudo capacitive electrode that operates by intercalation, similar to one electrode in a lithium ion battery. Or, there could be charge storage in an electrochromic polymer, such as a polythiophene. There are many faradic electrode materials that can be used with the double layer electrode, again using a large capacity ratio as previously described to obtain high cycle life.

(U//~~FOUO~~) One example of this type of device is a Hybrid Capacitor™ built by Evans capacitor (figure 5). This device uses the ruthenium oxide (RuO_2) as the faradic pseudo capacitive electrode and the tantalum oxide (Ta_2O_5) as the electrostatic electrode. This type of device allows the voltage to be controlled by the forming of the electrostatic electrode.

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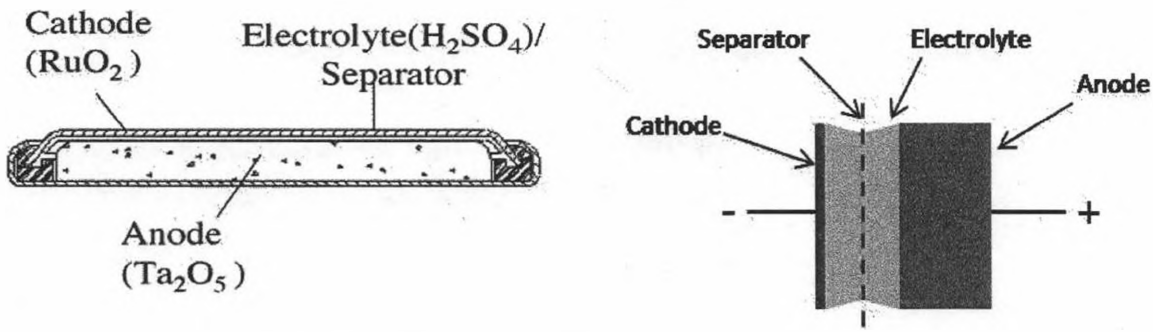

Figure 5. **(U//~~FOUO~~) Hybrid Capacitor Schematics Built by Evans Capacitor**

(U//~~FOUO~~) Typical performance characteristics of all types of electrochemical capacitors devices that make them different from batteries are a very steep discharge slope with the voltage going from initial voltage to half of initial to get 80 to 90 percent of energy out, which causes some problems in terms of control circuitry because most applications require a constant voltage or voltage in a narrow window. The other difference is cycle life. Most batteries have cycle lives in thousands of cycles. Most electrochemical devices have lifetimes in tens of thousands of cycles.

(U) Summary of Recent Work in Supercapacitors

(U//~~FOUO~~) The first cut at looking at recent work involved using a tool developed by Sandia that allows one to look at grouping of work in this area in several ways. As a first cut, all references that included the key words "electrochemical," "super," "asymmetric," and "symmetric" were gathered into a database. Results were gathered in figure 6.

(U//~~FOUO~~) For asymmetric devices, the work can be looked at both by country and year or by the type of work being done. Figure 7 shows that work has been done mostly in China, France, Japan, Australia, and Canada, with some work in the United States and India. The US work is only for use in medical devices; the Canadian work was done by the progenitor of this field, Brian Conway, and was very basic science-type work. The Australian work focused on the ultra battery, which is a combination of a lead acid and super capacitor and is now being manufactured in both the United States and Japan. Figure 7 shows that the most recent work is occurring in China.

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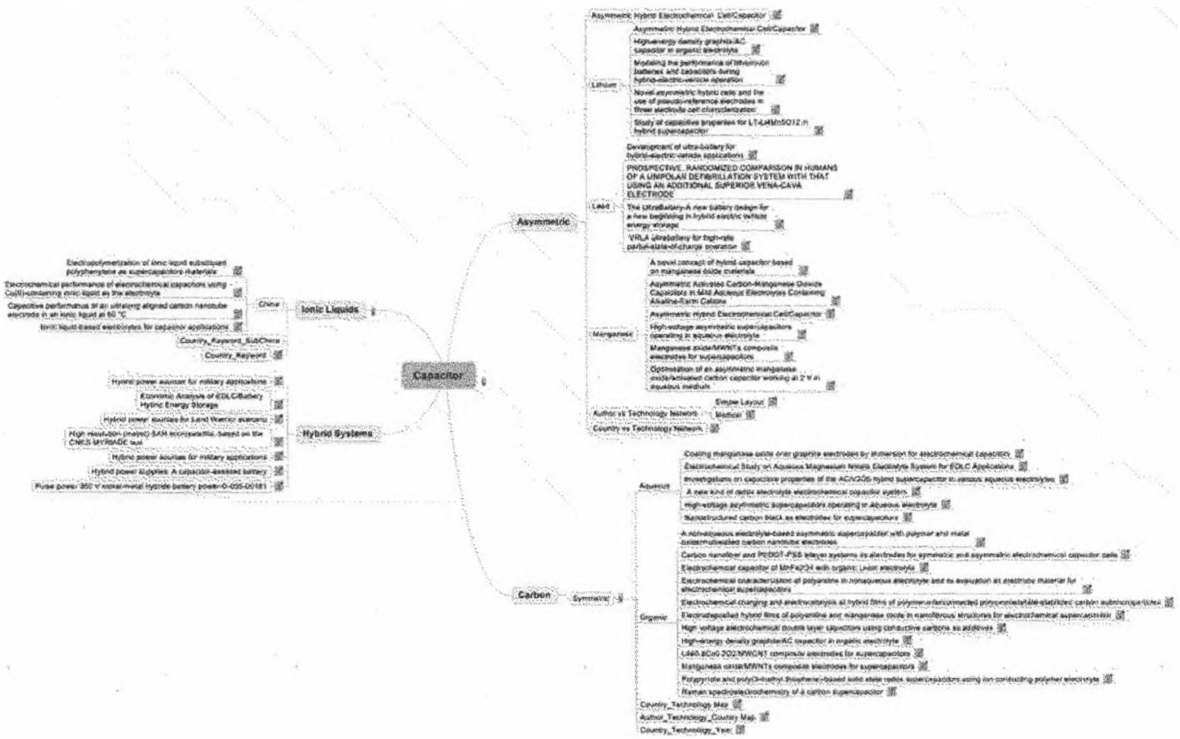

Figure 6. **(U//~~FOUO~~) Mindmap of Supercapacitors**

(U) China

(U//~~FOUO~~) The recent Chinese work focus on making for both electric vehicles and military applications. The Chinese have published review papers stating that they look at history and challenges for devices that include military applications, including those by authors from Tsinghua University and China Astronaut Center. Looking at the work, they cover the broadest range of possible technologies.

(U//~~FOUO~~) Spinel lithium manganate $Li_4Mn_5O_{12}$ nanoparticles were prepared by a very simple solgel method and tested as a cathode material in an asymmetric $Li_4Mn_5O_{12}$ alternating current (AC) supercapacitor in an aqueous electrolyte. The results showed that $Li_4Mn_5O_{12}$ annealed at 450 °C for four hours exhibited the best electrochemical capacitive performance within the potential range of 0–1.4 volts in a 1 mole (M) lithium sulfate (Li_2SO_4) solution. A maximum specific capacitance of 43 farads per gram (F/g), based on the total active material weight of the two electrodes was obtained for the $Li_4Mn_5O_{12}$/AC supercapacitor at a current density of 100 milliamperes per gram (mA/g). The capacitor showed excellent cycling performance and structure stability via 1,000 cycles.

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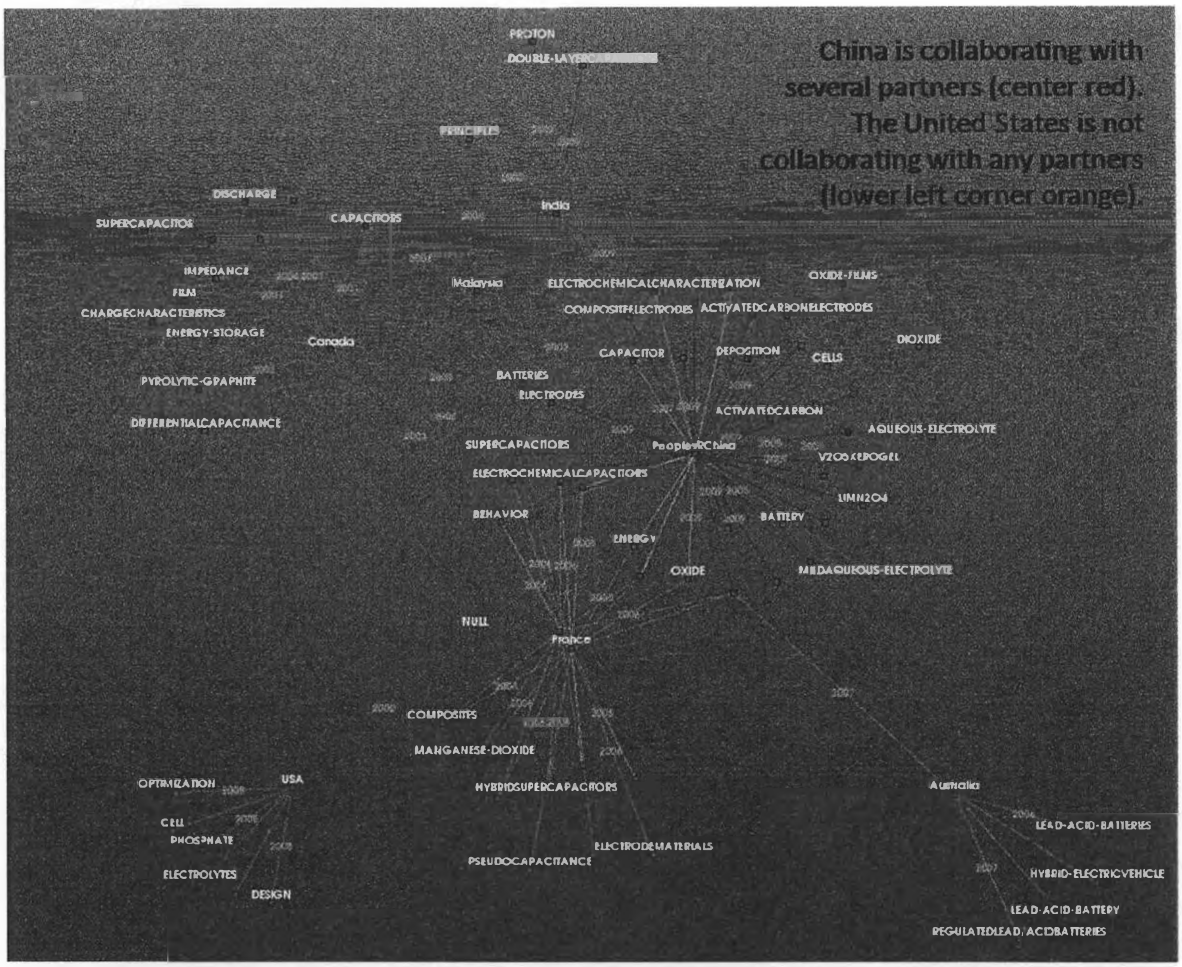

Figure 7. (U//~~FOUO~~) Interactions Map of International Collaborations in Supercapacitor Research

(U//~~FOUO~~) A novel asymmetric hybrid capacitor using $LiMn_2O_4$ and manganese oxide/carbon nanotube (CNT) nanocomposite as the positive and negative electrode materials, respectively, and 1M lithium percoplate ($LiClO_4$) in propylene carbonate as the electrolyte has been developed. To the best of our knowledge, this is the first reported assembly of an asymmetric hybrid capacitor with metal oxides for both electrode materials, and especially with MnO_2 as the negative electrode material. The discharge profile of the asymmetric hybrid capacitor shows a typical capacitive behavior with a linear slope. The asymmetric hybrid capacitor was able to deliver a specific energy as high as 56 watt-hour per kilogram (Wh/kg) at a specific power of 300 watts per kilogram (W/kg), based on the total weight of $LiMn_2O_4$ and MnO_2/CNT nanocomposite in both electrodes.

(U//~~FOUO~~) $LiNi_{0.8}CO_{0.2}O_2$ prepared by a rheological pretreatment gel-like method was used as the electrode materials for supercapacitors, and its electrochemical performance was investigated by galvanostatic charge/discharge testing. The almost linear discharge curves of the symmetric capacitors indicate that $LiNi_{0.8}CO_{0.2}O_2$ has a capacitive characteristic. Different multiwalled carbon nanotubes (MWCNT) and acetylene carbon black (AB) were used as the conductive additives of the $LiNi_{0.8}CO_{0.2}O_2$,

respectively. Under various current densities, the symmetric capacitors based on $LiNi_{0.8}Co_{0.2}O_2$/MWCNT composite electrodes have good capacitive and energy characteristics

(U//~~FOUO~~) A manganese oxide/multiwalled carbon nanotube (MWNT) composite was prepared by mixing manganese oxide and MWNTs through a means of ultrasonic vibration in ethanol solution. A non-aqueous hybrid supercapacitor using manganese oxide/MWNTs composite and MWNTs as positive and negative electrodes, respectively, has been designed and investigated constant current charge/discharge tests. The asymmetric hybrid capacitor has better capacitance and energy characteristics than those of the symmetric ones based on individual manganese oxide/MWNTs composite and MWNTs electrodes. The energy density of the hybrid capacitor can reach 32.91 Wh/kg at a current density of 10 mA/cm-cm^2 in 1 M $LiClO_4$ electrolyte, which is comparable to that of a manganese oxide/activated carbon hybrid capacitor.

(U//~~FOUO~~) Manganese oxide was coated on a graphite electrode by immersion. Durations for immersion were varied to control the amount of manganese oxide coated onto the electrode surface. Maximum capacitance of 556 millifarads per centimeter (mF/cm) was obtained in 0.5 M of lithiuym chloride (LiCl) and with better/superior conditions. In addition, cyclic voltammograms of the prepared electrode at different potential scan rates exhibited the approximately rectangular and symmetric current-potential characteristics of a capacitor. Furthermore, the chronopotentiometry charge-discharge curves of the electrode prepared at 80 minutes of immersion time with a constant current of 1 milliampere were symmetric and similar isosceles triangles, which demonstrate its high electrochemical reversibility and good stability. Finally, under scanning electron microscope, the surface of the electrode prepared at 80 minutes of immersion time and after 1,500 cycles of potential cycling revealed that a three-dimensional network of macropores appeared on large spherical grains.

(U//~~FOUO~~) Hybrid films of polyaniline (PANI) and manganese oxide (MnOx.) were obtained through potentiodynamic deposition from solutions of aniline and manganese sulfate ($MnSO_4$) at pH 5.6. The hybrid films demonstrated characteristic redox behaviors of PANI in acidic aqueous solution. Characterization of the hybrid films by x-ray diffraction (XRD) indicated the amorphous nature of MnOx in the films in which manganese existed in oxidation states of +2, +3 and +4, based on x-ray photoelectron spectroscopy (XPS) measurement. The hybrid film kept more than 90 percent of its capacitance after 1,000 charging-discharging cycles, with a coulombic efficiency of 98 percent. The specific capacitance of a symmetric capacitor using these hybrid films of PANI and MnOx PM120 as the electrodes is 112 F/g.

(U//~~FOUO~~) An amorphous vanadium oxide (V_2O_5) sample was prepared by a melt quenching method and used as part of a hybrid capacitor. The hybrid supercapacitor was fabricated with V_2O_5 positive electrode and activated carbon negative electrode in various aqueous electrolytes. The results showed that species of aqueous electrolyte, current density, potential range, and the active mass ratio of activated carbon to V_2O_5 had a great effect on the capacitive properties. The specific capacitance only slightly decreased with the increasing current density. When the mass ratio of activated carbon to V_2O_5 was increased to 3 to1, the capacitance of the activated carbon/V_2O_5 hybrid capacitor was similar to that of the V_2O_5/V_2O_5 symmetric cell.

(U//~~FOUO~~) The electrochemical characteristics and pseudocapacitive effects of Fe^{3+}/Fe^{2+} ion pair were investigated in an electrochemical capacitor system using porous carbon as electrode material and with sulfuric acid (H_2SO_4) solution containing Fe^{3+}/Fe^{2+} ion pair as electrolyte. The cyclic voltammetric results indicated that highly reversible electrochemical redox reactions of $Fe3^{+}/Fe^{2+}$ ion pair occurred within the nanopore structures of the porous carbon electrodes. Symmetrical charge/discharge cycles were achieved due to the existence of Fe^{3+}/Fe^{2+} ion pair, which effectively improved the capacity of the electrochemical capacitor system. The specific capacitance of the single electrode system reached 174 mAh, which is 109 mAh higher than that obtained using H_2SO_4 as the electrolyte. The charge/discharge mechanism of

Fe^{3+}/Fe^{2+} ion pair in the electrochemical capacitor systems was discussed, and a new type of redox electrolyte electrochemical capacitor was suggested.

(U) Australia, Japan, and United States

(U//~~FOUO~~) The UltraBattery, developed by CSIRO Energy Technology in Australia, is a hybrid energy storage device that combines an asymmetric super-capacitor and a lead-acid battery in single unit cells taking the best from both technologies without the need for extra, expensive electronic controls. The capacitor enhances the power and lifespan of the lead-acid battery as it acts as a buffer during high rate discharging and charging, thus enabling it to provide and absorb charge rapidly during vehicle acceleration and braking. The initial performance of the prototype UltraBatteries was evaluated according to the US FreedomCAR targets and was shown to meet or exceed these in terms of power, available energy, cold cranking, and self-discharge set for both minimum and maximum power-assist hybrid electric vehicles. Other laboratory cycling tests showed a fourfold improvement over previous state-of-the-art lead-acid batteries under the RHOLAB test profile and better life than commercial nickel/metal hydride (NiMH) cells used in a Honda Insight when tested under the European Council for Automotive R&D Hybrid Electric Vehicle (EUCAR HEV) profile. As a result of this work the Furukawa Battery Co., Ltd. in Japan built a set of 12 12-volt modules and were fitted them into a Honda Insight instead of the NiMH battery by Provector Ltd. The battery pack was fitted with full monitoring and control capabilities and the car was tested at Millbrook Proving Ground under a General Motors road test simulation cycle for an initial target of 50,000 miles, which was extended to 100,000 miles. This was completed on 15 January 2008 without any battery problems. Furthermore, the whole test was completed without the need for any conditioning or equalization of the battery pack. A US company is in the process of building a plant to build this technology in the United States.

(U) Korea

(U//~~FOUO~~) A novel asymmetric hybrid capacitor using $LiMn_2O_4$ and MnO_2/ CNT nanocomposite as the positive and negative electrode materials, respectively, and 1 M $LiClO_4$ in propylene carbonate as the electrolyte has been developed, resulting in the first reported assembly of an asymmetric hybrid capacitor with metal oxides for both electrode materials, and especially with MnO_2 as the negative electrode material. The discharge profile of the asymmetric hybrid capacitor shows a typical capacitive behavior with a linear slope. The asymmetric hybrid capacitor was able to deliver a specific energy as high as 56 Wh/kg at a specific power of 300 W/kg, based on the total weight of $LiMn_2O_4$ and MnO_2/CNT nanocomposite in both electrodes. These results clearly demonstrated a superior performance of this new type of capacitor with a higher specific energy compared to other types of asymmetric hybrid capacitors.

(U) Hybrid Power Systems Development

(U//~~FOUO~~) Here, we explored how an electrochemical capacitor system might be utilized in a hybrid system. It was found that only the Chinese and United States publish in this area, and the Chinese looked at economics of the system. The United States is much more interested in the military applications.

(U) Future Trends in Supercapacitors

(U//~~FOUO~~) From reviewing the available work several conclusions can be drawn. Many countries have done some work in these areas. For most countries, the work seems limited to either basic understanding of how this technology works (Canada and the United States) to developing single types of technology. The Chinese work is very different. Their work covers the spectra from looking at the history of the development as well as the economics of the technology to very basic research that could lead to very new high performing devices. It was the only country that worked in developing both new electrode materials and new electrolytes. They also were working in the next step, which is cell configuration. The

fact that they were the only non-US country to state its need as military leads one to believe it has specific needs. However, given that China is publishing more on this topic than anyone in recent history, it appears that the Chinese are still exploring options.

(U) Mechanical Energy Storage

(U) Introduction to Mechanical Energy Storage

(U//~~FOUO~~) Energy storage via mechanical means is the oldest energy storage mechanism actively engineered by man. The use of pre-stressed wood, early potter's wheels, and eventually metal springs all demonstrate mechanical energy storage to perform useful work. Early clocks, which used the potential energy stored in elevated reservoirs of water to induce motion, were common throughout ancient times. The manufacture of metal springs, with their relatively more efficient and compact storage of potential energy, enabled more complex clockwork timing in the 1400s. During the industrial revolution, flywheels were often incorporated into steam engines and early manufacturing equipment. Though these storage elements have been used for hundreds of years, researchers have generally eschewed mechanical energy storage in favor of electrochemical storage. The reasons for this are varied, but include the lack of moving parts on a battery, the capability to store energy for a relatively long duration, and the portable nature of electrochemical cells. While still largely confined to niche applications, active research in the mechanical energy storage field is ongoing.

(U//~~FOUO~~) For large-scale energy storage, a number of different mechanical storage techniques have been investigated for electrical utilities and industrial concerns. Compressed air energy storage is a technique that uses off-peak electricity, usually generated in the evenings, from the grid to compress air and store it in an underground cavern or other vessel. When needed, the high-pressure air is released and directed to spin a turbine. Pumped hydroelectric storage is a similar system that uses water in an elevated storage reservoir to drive a turbine. Both of these approaches have been pursued due to economic concerns stemming from peak energy usage costs.

(U//~~FOUO~~) Other recent applications for mechanical energy storage include the use of flywheels for satellite pointing, backup power sources, electrical cars, and output smoothing for wind turbines. Compressed vessels of air or other gasses have also been researched to provide the motive force for small, compact vehicles with zero or near zero environmental emissions. Commercial vehicles running with either of these technologies are in low volume production, as neither technology has reached the efficiencies and economic requirements for high volume production.

(U//~~FOUO~~) Mechanical energy storage for small-scale applications, such as providing energy for a single sensor or small system, will be the focus for the rest of this section. With the advent of micro-electromechanical systems (MEMS) and low power complimentary metal-oxide-semiconductor (CMOS) sensors, the reduced power requirements to operate relatively sophisticated systems has generated renewed interest in the development of mechanical energy storage technologies. Technologies such as miniaturized or micro-flywheels and MEMS-fabricated springs, or other pre-stressed structures, have been active areas of research over the past few decades. With the advent of nanofabrication and other "nano" material technologies, ongoing research on the use of materials such as carbon nanotubes has also appeared in the patent and technical literature.

(U) Flywheels

(U//~~FOUO~~) At the simplest level, a flywheel is a device that stores kinetic energy in the high-speed rotation of a cylindrical or hoop-shaped mass often called a rotor. Modern, demonstrated laboratory flywheel systems have operated at rotational rates upwards of 60,000 revolutions per minute (rpm). These high speeds of rotation allow even a relatively small or light rotational mass to store large amounts of kinetic energy. In most cases an electric motor is used to spin the rotor to speed, though all-mechanical

designs featuring continuously variable transmissions for the automotive industry, to recover energy during breaking, are under development. When energy is needed, it is extracted from the flywheel system by treating the spinning rotor as the shaft of a generator, in which case the rotor slows but produces electricity as it does. The energy density of flywheel systems is dependent on the sophistication of the technology, but energy storage densities of 30 joules per gram (J/g) have been reported for steel rotor systems, while composite rotor systems have demonstrated energy densities comparable with lithium ion batteries at ~500 J/g. Flywheel systems are relatively insensitive to temperature swings, quick to charge and discharge, not harmed by "deep discharge," long lasting (about 10 years), have a greater than 90 percent charging efficiency, and have a very low loss of stored energy with time. The overall sizes of such systems are typically on the order of a few hundred kilograms or larger, though designs for cars are sized at the 25-kg level. Recent research has demonstrated the utility of using MEMS fabrication methods to design micro-flywheel systems. Work on these systems is preliminary, but seems promising.

(U//~~FOUO~~) Early rotors were made from metals, such as high-strength steels, while later designs have featured lighter, carbon graphite reinforced composites. Switching to lighter composite materials dropped the overall weight of these systems and allowed for an increase in the rotor speed from thousands of rpm for metal systems, to the present day value of tens of thousands of rpm. This speed increase is made possible by the increased tensile strength of the newer composites, resulting in a net increase in the energy density of flywheel systems. Composite materials also have the advantage of rapidly disintegrating into small, lightweight pieces when the rotor is damaged as opposed to the high velocity metal shrapnel that is formed when a conventional metal rotor is damaged.

(U//~~FOUO~~) In order to achieve the energy densities of state-of-the-art designs, there are a number of technical advancements that a system must feature. These system requirements include magnetic bearings to reduce friction on the rotor and an evacuated chamber to house the rotor. Many groups are experimenting with high temperature superconductor materials to replace standard magnetic bearings, though thus far no commercially available high temperature superconductor system has been shown. High temperature superconductor bearings would be able to support and stabilize a larger rotor at higher rotational speeds, compared to traditional magnetic bearings.

(U) Micro-Mechanical Springs

(U//~~FOUO~~) The fabrication of highly miniaturized MEMS springs and other structures that store mechanical stress have been pursued by a few groups throughout the world, though the majority of the work has been done in the United States. MEMS springs formed from single crystal silicon or polysilicon have been fairly common in the literature for use as structural supports or restoring springs for shuttle masses in accelerometers and resonators. The use of these structures for the sole purpose of energy storage, however, is fairly rare. One reason is likely the relatively low energy storage density found in steel springs, which is around 1 joule per cubic centimeter (J/cc), and thus they offer a significantly lower energy density than a lithium ion battery. Springs, whether fabricated from MEMS structures or not, have a common disadvantage in that their force profiles can vary with displacement if the spring is based on a bent beam. Since many MEMS spring designs are beam-based, this variance could be an issue for some applications. Also, the force output of springs, assuming Hook's law performance, linearly changes with spring displacement meaning that the force output from the spring decreases as the spring unwinds. Mechanical compensation mechanisms, often found in a miniaturized form in mechanical clocks, have been developed to produce flattened force profiles, though these mechanisms tend to be fairly complex. The author has seen no effort to replicate them in MEMS technologies thus far.

(U//~~FOUO~~) Investigation of nanostructures, such as CNT carpets or CNT ropes, for use as energy storage devices has been an active, though somewhat speculative, area of research for a number of years. These nanostructures have shown themselves to be extremely resilient and strong, thus allowing the storage of greater mechanical stress than typical spring materials, such as steel. Extensive theoretical calculations have shown this material's suitability for energy storage, but the practical difficulties of winding and

forming a high-quality CNT rope or carpet have not yet been addressed. Recent work in the United States has demonstrated that CNT materials have been developed that have recorded energy storage densities on the order of 0.2 J/cc.[1] This energy density is off the theoretical maximum because of the imperfect nature of the tested material. If the energy density of the springs is measured in terms of unit mass, then the value of 5 J/g exceeds the energy density of steel springs, and yet is an estimated three orders of magnitude below the maximum predicted energy density of CNT materials. The predicted energy density value of an ideal material made from defect-free nanotubes would be 200 J/cc, which is on the scale of chemical battery energy storage.

(U//~~FOUO~~) Other elastomeric[2] and silicon structures[3] for energy storage have been developed by US researchers. The literature representing this work did not record the overall size of the systems necessary to support this stored energy, so energy density estimates are difficult to make, but estimates of energy density would be approximately 70 nanojoules per gram (nJ/g) and 163 nJ/g, respectively. While neither of these published works sought to maximize energy density, it does illustrate the relatively poor energy storage capabilities of simple spring mechanical systems. The advantage that spring systems do have is that they discharge their stored energy extremely rapidly, which could be useful in some applications.

(U) Surface Tension Energy Storage

(U//~~FOUO~~) Another mechanism of mechanical energy storage that has been used in the literature is the energy inherent in surface tension. This energy represents the higher energy available at the surface of a material, usually a liquid, compared to its interior molecules. The magnitude of the surface energy is dependent on the two materials that form interfaces with each other, and thus a droplet will minimize its surface tension by wetting, or interacting, with a material that has a lower available surface energy. This available energy is extremely small, but has been harnessed for the self-assembly of nano- and micro-structures. The surface energy of water in air is approximately $7.2e^{-5}$ J/cm^2, and so the energy density to be harvested from a cubic centimeter of fluid is significantly lower than a chemical battery. It is conceivable this energy could be harvested to mechanically actuate switches, for instance, especially when coupled with a material that undergoes a phase change at a desirable temperature point.

(U) Foreign Country Progress in Mechanical Storage

(U) Australia

(U) Micro-Mechanical Springs

(U//~~FOUO~~) The Commonwealth Scientific and Industrial Research Organization has produced work on the subject of CNT-based ropes and fibers.[4] The group frequently collaborates with faculty at the University of Texas. Their work is particularly interesting because they focus on manufacturability in the creation of their CNT-based material. They use densely packed CNT forests, or mats, as the starting material for their CNT ropes. The starting material is grown to have the property that individual nanotubes will stick to one another as they are removed from the CNT forest. This sticking allows a continuous string of adhered tubes to be pulled together, and woven using conventional fiber fabrication technology. The group has thus far created 10-µm thick fibers that have breaking strengths on the order of 27 J/g, which is becoming comparable to the breaking strength of Kevlar at 33 J/g. Their techniques may be applicable to the eventual construction of CNT ropes appropriate for mechanical energy storage.

(U) China

(U) Flywheels

(U//~~FOUO~~) The Chinese research community appears to not be focused on micro-flywheel systems, but rather more miniaturized systems appropriate for satellite applications. No Chinese technical literature was located showing a Chinese team of researchers working on active prototype fabrication of micro-flywheel systems. Interest seems to be placed on miniaturizing conventional systems with HTS technologies. Examples of contemporary work found in China include a conference paper out of the Applied Superconductivity Laboratory at Southwest Jiaotong University.[5] This particular work shows an overall system size of 610 mm × 500 mm. It uses conventional HTS materials to levitate a 2.4-kg mass, at a maximum speed of 3,000 rpm. Neither spin-down time nor power outputs have been quoted in the work, though the authors did note that there were severe resonance issues at certain speeds, which is likely from non-uniformities in the magnetic field. Another group at the Institute of Electrical Engineering, which is attached to the Chinese Academy of Sciences, has published extensively on HTS bearings, windings, and the construction of magnet systems. More than 50 papers have come out of this institute on HTS and another 16 have been published on flywheel technology. The technology displayed appeared to be for conventional-scale systems, but nevertheless the group possesses a good technical grasp of the components necessary to begin development of a miniaturized or micro-system. In 2009, a group that has published in Chinese-language technical journals on flywheel technology, released a computational modeling paper on micro-flywheel design.[6] Members of this group, who have worked on conventional flywheel design since 2004, work out of the Changchun Institute of Optics, which is attached to the Chinese Academy of Sciences through the State Key Laboratory of Applied Optics. While only a preliminary modeling study, this paper likely indicates another group within China with an interest in the development micro-flywheel systems or technologies that can be used in the development of them.

(U//~~FOUO~~) An immense amount of work has also been pursued on MEMS gyro applications in China. Some of the engineering principles applied to spinning disc-style MEMS gyros can also be applied to micro-flywheel systems. A group from the National Key Laboratory of Nano/Micro Fabrication Technology at Shanghai Jiao Tong University has published on the computational modeling of such a gyro system.[7] Earlier work by some of their team members also explored the use of LIGA processing to create micro-machined rotors using conventional microfabrication techniques.[8] A 2006 paper from this institution demonstrates a working MEMS gyro system, though one with a slow disc rotation of 4,000 rpm.[9] Their latest effort in 2009 further explores the LIGA rotor concept and studies different system control techniques.[10] The basic principles of disc levitation and control can be easily applied to micro-flywheel construction. This steady progress indicates this group is likely capable of developing a micro-flywheel system.

(U) Micro-Mechanical Springs

(U//~~FOUO~~) Some of the earliest work on CNT fiber creation was done out of the Fan group at Tsinghua University. Their early paper on the subject demonstrated the possibility of first drawing a continuous string of nanotubes from a densely packed CNT array.[11] Since that early work, the group has averaged more than a dozen papers or conference proceedings per year on their work with CNT and CNT-based materials. An active area of inquiry for the group is constructing dense 2-D papers made by crushing mats of nanotubes into contiguous films.[12] While there was no immediate evidence of turning this expertise towards the construction of mechanical storage material, this group would be an excellent candidate for work in this area.

(U) Japan

(U) Flywheels

(U//~~FOUO~~) Collaboration between the Japanese company Tokimec Inc. and a University group led by Masayoshi Esashi has produced a high-quality spinning disc gyro system.[13] The system was made with conventional microfabrication techniques, and features a 4-mm diameter ring rotor fabricated from deep plasma-etched silicon. This is a sophisticated design constructed from a die 16 mm^2 on a side, which has been packaged into a hermetically sealed container of a similar size to the original die. The system was tested to a rotational speed of 12,300 rpm. This work builds on the group's previous efforts that used a solid disk for the rotor instead of the ring.[14]

(U) Micro-Mechanical Springs

(U//~~FOUO~~) Extensive work has been done in Japan on CNT and other carbon structures. The work of the Motojima group out of the Department of Applied Chemistry at Gifu University shows particular interest. The group has published more than 30 papers since 2005 on the subject of CNT microcoils,[15] carbon structure mechanics, CNT growth, and the integration of ceramic and carbon structures within polymer. The group's publishing peak was in 2006, when they had 15 papers and conference talks recorded in the Engineering Index. The group is well-versed in the mechanics of carbon structures and has experimented with methods to increase their mechanical properties. In particular, their early work with carbon microcoils had identified the possibility of using these structures as springs and actuators. If they chose to work with the material in an energy storage application, they would likely be well-equipped to make progress.

(U) Russia

(U) Micro-Mechanical Springs

(U//~~FOUO~~) In association with US researchers, early work was done in this country on the compressibility of CNT materials.[16] While the authors did not speculate on uses for the material, outside of a general observation of the material's utility in composite structures, they did analyze the behavior of CNT materials under varying pressures and load durations. As expected, variability in the material's porosity caused variation in the energy storage, with unpurified material exhibiting much greater porosity than purified material. The authors also speculated on the energy storage mechanisms of the tubes, with their eventual conclusion being that CNT carpets, with individual tubes tangled together, act as highly linked, reversible springs. After this initial work on CNT energy storage, there are no further occurrences of the Russian participants within this group continuing to work on CNT springs.

(U) South Korea

(U) Flywheels

(U//~~FOUO~~) This country appears to be a leader in research on miniature and micro-flywheel technologies. The majority of the work done in this area comes from groups within two technical institutions: Chungnam National University and the Korea Advanced Institute of Science and Technology, with HTS material supplied by the Korea Electric Power Research Institute. These groups actively collaborate together and appear to have done so since before 2005 when their first paper on the subject was published with Eunjeong Lee.[17] This collaboration with the groups from Chungnam National University and the Korea Advanced Institute of Science and Technology appears to be her last paper on this particular topic.

(U//~~FOUO~~) Since that time the group has published approximately 10 papers in the area of micro-flywheel design, fabrication, modeling, and testing. The group appears to have borrowed heavily from the

earlier efforts of Eunjeong Lee who worked at the University of Texas in San Antonio, along with collaborators from the University of Virginia and the NASA Johnson Space Center. [18] Her earlier work in the United States with NASA concentrated on the use of magnetic and HTS bearings for a variety of satellite and telescope applications.

(U//~~FOUO~~) Their last published work on the subject appeared to be in May 2008. This work detailed a laboratory system with HTS bearings, a gold electroplated planar stator, and an aluminum flywheel. Once the system is cooled below 72 kelvin, the flywheel levitates between the stator and the HTS bearings with a high lateral stiffness that keeps the flywheel confined even at high spin rates. The team has exhibited levitation of the flywheel with a 7-mm separation between the flywheel and the HTS bearings. The group has achieved a flywheel rotational speed of ~51,000 rpm with this setup, and produced 50 megawatts of power as a result. The spin-down time of their setup, the time the flywheel takes to cease spinning with no power applied to it, was 200 minutes. A state-of-the-art macro scale systems has a spin-down time measured over many months, indicating large inefficiencies still remain within their system. That stated, the group appears to have made steady progress, with work from 2005 demonstrating flywheel rotational rates of 12,000 rpm and work from 2006 demonstrated 38,000 rpm. This progress was mainly due to better understanding of the non-uniformities of the system's magnetic fields and the use of HTS bearings. Their current system size in not stated, but the core of the setup appears to be soup-can sized.

(U//~~FOUO~~) The group's stated technical approach is aimed at providing a micro-flywheel energy storage system for miniaturized satellite systems. In this instance the torque generated by a rotating mass is useful to assist in satellite pointing. As a result of this targeted application, the technical progress they have made emphasizes using the vacuum of space in place of an evacuated enclosure. This likely does not prohibit terrestrial emplacement, though it would require additional research and development be put into the device packaging. The group also seems to wish to use the space environment to cool the HTS bearings they are developing for this application. The cooling required for the superconducting material is amongst the impediments they would face for a minimized device footprint for terrestrial application.

(U) Taiwan

(U) Surface Tension Energy Storage

(U//~~FOUO~~) Much work has been done in this area by groups in Taiwan, as they are seeking a replacement for traditional pick and place technology used in circuit board manufacturing. The Chiang group from National Tsing Hua University has produced several papers on this subject in recent years. Their latest work developed a comprehensive, computational model that was used to optimize the physical properties of the micro-part, lubricant, and medium (air or water). [19] They also have previously-published work detailing their experimental efforts to self-align parts using surface tension.

(U) United Kingdom

(U) Flywheels

(U//~~FOUO~~) Researchers at the Interdisciplinary Research Center of Superconductivity at Cambridge University have worked on a variety of flywheel and HTS-centered subjects. In 2006, the group was actively researching the properties of levitation in micro-systems for the purpose of creating magnetic bearings and micro-flywheel systems. [20] At that time, the group had demonstrated the ability to levitate a planar device with HTS bearings. They additionally published their computational modeling approach, and the techniques necessary to fabricate the rotor structure and HTS bearings. Subsequent work in the area of micro-flywheels is not seen in the literature for this group, though they continue to publish about macro-scale commercial systems and HTS bearings. In another paper from 2006, the group collaborates with researchers from the Institute of Electrical Engineering, which is attached to the Chinese Academy of Sciences. [21] That group has historically published on HTS technology extensively.

(U) Surface Tension Energy Storage

(U//~~FOUO~~) RRA Syms was one of the first proponents of the surface-tension self-assembly technique with work on MEMS torsion mirrors and the assembly of 3-D MEMS structures.[22] Since the initial work in 1993, his group at the Imperial College London has published almost yearly on the subject into the present day. The primary focus has been on using the surface tension forces to provide rotational energy for the movement or assembly of a component. Syms has collaborated recently with other entities like the Samsung Semiconductor R&D Institution in South Korea.

(U) Future Trends in Mechanical Energy Storage

(U//~~FOUO~~) A review of the available literature indicates that micro-flywheel technology shows the most promise for developing a miniaturized, mechanical energy storage system. In addition to the higher energy densities of such a system, micro-flywheels also have the advantage of providing a direct electrical power output, as opposed to the other technologies presented here, which provide only mechanical power output. While the energy densities of micro-flywheel systems could be quite high, on the order of 410 J/cm^3 (in a package ~50 mm is diameter and ~10-mm thick), as predicted in a paper on the subject from 2003,[23] significant technical hurdles remain for the systems to be used in terrestrial applications. Issues that remain include vacuum packaging of the rotating elements and cryogenic cooling of the HTS bearings. Of note on the last point, miniaturized rotor systems may not need HTS bearings to achieve high-quality stabilization and confinement. More traditional electrostatic or magnetic levitation may be sufficient for micro-flywheel systems. If this is the case, accepting inefficiencies in the micro-flywheel design in exchange for the miniaturization and maintenance advantages of dispensing with cryogenic cooling might be an advantageous trade-off. As macro-scale flywheel systems are already being used for power management, power backup, and in regenerative breaking systems for vehicles, it is likely that additional technology from these maturing commercial applications will be applied to the miniaturized power problem with some success.

(U//~~FOUO~~) Extrapolating the progress of this technology into the 5- and 15-year timeframes is difficult, as precise measurements of current energy densities are not available in the literature. While progress on planar rotor speeds has been made over the last ten years, they are still an order of magnitude off what miniaturized systems would require in order to achieve the high energy densities quoted in the literature. Using the South Korean group as a benchmark, we can estimate that rotor speed increases will generally continue to fall off, thus we would not expect the high speeds over 100,000 rpm to occur until closer to the 15-year mark. With the lower speeds, we would also expect a commensurately lower energy density, as the stored energy of the system goes as the square of the angular velocity.

(U//~~FOUO~~) For the other mechanical storage techniques, such as the storage of energy in silicon beams, liquid surfaces, elastomers, or CNT fibers, this area of investigation and technical progress will likely continue at a low rate due to the low energy densities that these systems can store. Spring-based energy storage will probably only be useful for niche applications. The exception to this statement is likely to be the storage of energy in bundles of CNT fiber. Given the interest of researchers around the world in developing ultra-strong CNT fibers and composites, it is likely this field will see active research and progress in the coming years. A proposed system from the literature that uses a CNT bundle to store mechanical energy and then convert it into electrical energy using piezoelectrics, estimates a stored energy of 60 joules for a millimeter-scale system.[24] While the specific energy density was not published, the authors felt such a system would be competitive with chemical-battery storage densities. If the author's assumptions and calculations are correct, given the relatively rapid rate of progress on CNT fiber and rope construction, one would expect such a system to be achievable by the 5-year time frame with a degraded performance, and a near chemical-battery storage possible within the 15-year timeframe.

(U) Radioisotopic Systems

(U) Introduction to Radioisotopic Conversion

(U//~~FOUO~~) While not exactly an energy storage device, systems that link a conversion system to a long-lived, radioisotopic power source can operate at low levels for such a long time that they practically can be considered as "infinite" energy storage devices. These devices are almost always characterized by low rate capability, since both the power source (the radioisotope) and the converter (either thermal, photon based, or direct conversion) have a finite upper limit on the rate they can generate and convert useful energy. Since thermal conversion systems have been discussed previously, this study will limit the scope to only those systems that rely on either direct conversion of decay products into electricity, or rely on conversion of the decay product into photons or charge, rather than phonons.

(U//~~FOUO~~) Radioactive decay releases one of three principle types of particles, either a positively charged helium nucleus (an "alpha" particle), a negatively charged electron (a "beta" particle), or an uncharged neutron. There is also often the release of energy in the form of a high energy photon, or "gamma" ray. Of all of these releases, the principle conversion methods work with either alpha or beta particles. Harvesting then either takes advantage of the high kinetic energy often released with these particles (often in the tens to hundreds of thousands of electron volts), or uses the charge itself. Converters that make use of the charge on the particle itself are called primary converters; those that take advantage of the kinetic energy are called secondary converters. The most common type of secondary converters utilize the alpha particle self heating of materials, such as plutonium and uranium to create a thermal gradient between the radioisotope and the surrounding environment. This heat gradient can then be converted into electrical energy, usually using thermoelectric materials to convert the heat. Because of the architecture of thermoelectric systems, the form of the output energy (voltage and current) can be designed to support a wide variety of loads, and it is this flexibility that has made it a workhorse of radiolytic systems to date.

(U//~~FOUO~~) However, there are some inherent limitations to secondary converters. Heat conversion is limited in efficiency by the Carnot efficiency, and there is a separate inefficiency associated with the materials themselves. This efficiency improves with a higher heat gradient and higher fluence of heat, but higher heat fluences also imply more radioisotope in use, which increases the need for shielding to protect against other decay products (neutrons and gammas) from causing harm to surrounding materials, either electronic, materials, or biological elements. These systems scale poorly because smaller scale heat systems have a larger surface to volume ratio, which leads to a more difficult problem in managing the heat down the thermoelectric legs.

(U//~~FOUO~~) In contrast to secondary systems, primary systems seek to use the charge of the emitted particle itself to do work or generate a current directly. Either the particle's charge is used directly to create charge on a plate and create electrostatic mechanical attraction, or the charged particle is used to irradiate a semiconducting p/n junction to generate electron/hole pairs, similar to photon irradiation for photoelectric devices. One of the largest challenges of the former is that all of the kinetic energy of the particle is lost, and only the minor energy of the actual charge itself is used to create power. For the latter type of system, the main drawback is that, unlike photons, there is sufficient energy in the irradiating particle to cause crystal structure damage to the semiconductor, resulting in a decrease in performance of the device as the total accumulated dose within the semiconductor increases. There are active research areas in all of these devices within the United States, but they are somewhat specific and concentrated under individual research groups. Similarly, foreign nations are starting to publish in these areas, but like in the United States, the work seems to be relatively isolated to a small handful of researchers in each specific area.

(U//~~FOUO~~) Finally, before discussing individual technologies and individual countries, it would be worth distinguishing between power sources that have been realized, or at least have the potential to be realized,

from power sources that are not in a position to yield useful power. Energy storage systems, at least practical ones, typically generate at a specific voltage, and maintain that voltage irrespective of the amount of current drawn (within an operating window of current). The Zn-MnO_2 alkaline battery is a classic example of this; it provides 1.5 volts, whether it is providing a microamp or 100 milliamps of current. The energy density, then, is reported as a number of amps for a number of hours; amp-hr of energy (at a given voltage). Power sources that are mature enough to report energy density in these terms are more than likely mature enough to have engendered a prototype capable of being measured in this way. In contrast, more esoteric power sources that are relatively immature can be spotted by the way "power" is reported. Typically, a voltage without a current will be reported, or an open circuit voltage and short circuit current will be reported. What this implies is that the technology has a significant amount of voltage drift under different loads, and therefore is difficult to implement into a real power source application.

(U) Thermoelectrics for Heat Conversion

(U//~~FOUO~~) Thermal converters take the self heating from a radioisotope and convert this heat energy into electricity (secondary converters). Of these systems, thermoelectrics are the most common power source system available, and a large number of countries have at least some work going on in making these systems into practical devices. Since they have application in the medical community for pacemakers, as well as small, long lived power sources for commercial applications, most of this work can be found in the open literature. Germany has a relatively large number of groups working in this area specifically in the area of implantable pacemaker power systems, and is very advanced in reducing these power systems to practice. Reidemeister, et. al.[25] showed that work in this area in Germany was progressing towards application as early as 1973, and several other papers from that period also support a significant effort towards realizing a plutonium-238-based power supply. Supporting work several years later from Germany also showed that secondary effects on performance and performance improvements were being considered, which likely was indicative of a fairly high degree of sophistication.[26,27] More recent publications are lacking in this area, however, with no real publications of any note coming after around the mid 1980s, which indicates that a level of maturity for practical application (at least with plutonium) had been reached, and additional research in this area was discontinued due to health concerns from radiation exposure from the source, along with improvements in the energy density of the electrochemical systems, and the ability to recharge these systems within the body.

(U) Alphaphotovoltaics for Direct Conversion

(U//~~FOUO~~) These primary conversion devices seek to convert the energy of an alpha particle emission directly into electricity, without relying on the alpha particle colliding with the lattice of the emitting material and generating heat (which is then harvested with a thermoelectric device). Within the United States, the most prolific author in this area seems to be R. Raffaelle at Rochester, now within a spin off center of NanoPower Research Laboratories.[28, 29] Most of this work centers on using radiophosphors to convert the energy from emitted alpha particles into photons within a radiation tolerant matrix (preferably one that is amorphous, to overcome the radiation damage issues). The emitted photons then are absorbed by a traditional photovoltaic to be converted into electricity. Outside of the United States, the equivalent researcher to Raffaelle in this area seems to be V M Balebanov, from the Institute for Space Research in the Russian Academy of Sciences. While the bulk of his work does not involve radiophosphor conversion like Rafaelle's work, there is nonetheless a significant contribution in understanding ion/solid interactions with regard to generation of power. A majority of the treatment is theoretical in nature, with direct energetic charged particle interaction with the solids generating a given charge distribution in a current generating device.[30,31,32]. Much more recently, in 2003, this affiliated group (see the interaction matrix in figure 8) first makes reference to a radioisotopic battery in their publications.[33]

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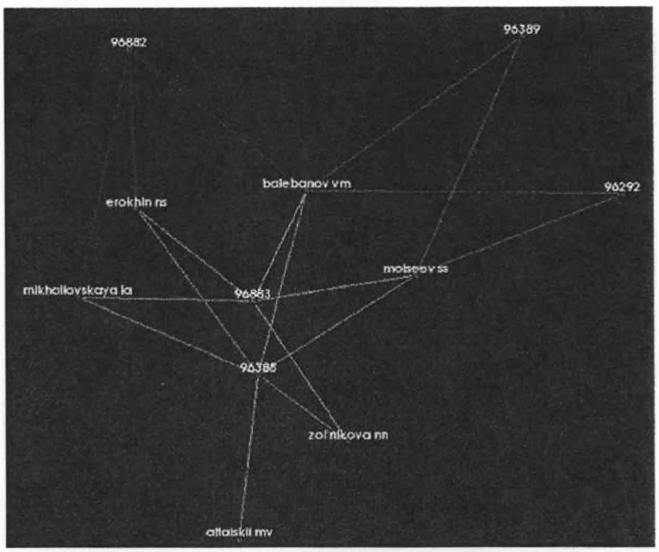

Figure 8. **(U//~~FOUO~~) Interactions Diagram for V.M. Balebanov, Working in the Area of Radioisotopic Direct Conversion (Numbers are Individual Papers; Names are Collaborators)**

(U//~~FOUO~~) In this paper, the application of ionic interaction with solid state plasma films for secondary emission is discussed, and it is possible, given the description of the work, that this is also a radiophosphor study. Interestingly, after 2003, no more recent reports from this community were forthcoming. Given that Balebanov has been working since the mid 1970s in this field and the technology's state of maturity in 2003 from their conference paper, it may be that Balebanov left the field or retired, rather than the technology matured to a usable point.

(U//~~FOUO~~) At the time of Belabanov's work, a highly cited reference book was also published that listed radioisotopic microbatteries as the title, and reviewed a number of polymers, radiophosphors, and circuit analyses for upconversion of primary and secondary radiolytic systems through the CRC Press.[34] This is referenced in the most recent of Balebanov's papers, and includes a number of practical considerations for how to turn the emitted primary radiation into power, albeit at very low (nanowatt) levels.

(U) Betavoltaics for Direct Conversion

(U//~~FOUO~~) Direct conversion of a fast emitted electron can either be harvested directly for the charge, or as a generator of secondary emissions, if the energy is sufficient. Both of these are considered primary conversion devices, as the self-heating from beta sources is, in most cases, vastly inferior to alpha emission sources. Within the United States, the betavoltaic studies are largely dominated by two groups; Betabatt, Inc. for radiovoltaic systems, and the Lal group at Cornell for microelectromechanical conversion. Radiovoltaic systems (or betavoltaic systems) use the beta particle as a generator of hole-electron pairs in a semiconductor, analogous to a photovoltaic device. Materials work in this area[35] is to improve the resistance to radiation damage of the converter device. Theoretical work is happening in Russia[36] and source materials (notably tritium) are being researched in Canada.[37] Of note is the researcher N P Kherani, who appears in both the area of increasing the performance of the converter material and in researching storage of the radioisotope source. None of these systems are advanced beyond the research phase, however, and Betabatt seems to hold a number of the patents surrounding this technology.

However, the energy density of such systems is also quite low, and the lifetimes of the systems are also subject to debate, and it is unlikely that these systems can generate power in a form that would be useful to a system currently. There is also a minor Chinese effort in this area, with a few papers from Guo, et al, which address the use of porous silicon for the actual junction device in an effort to suppress degradation of the device under irradiation.[38]

The other form of betavoltaics involves trapping the charge of the beta particle within a material, and using the built up field of the charge to generate mechanical motion. First demonstrated by Lal, et. al.,[39] this method uses emitted beta particles to develop a potential difference (often a large one, up to the kinetic energy of the particle) between the radioisotope and an electrically isolated cantilever. Charge differential generates electrostatic force, which moves the cantilever toward the radioisotopic source. Once snap in of the gap occurs, the electrostatic potential difference is discharged, and the cantilever is restored to its original position, where the slow charging by electron bombardment begins again. In this field, the Chinese have been particularly active, with several recent publications by a few authors of interest. Li Sun at the Northwester Polytechnical University in Xi'an seems to be the focal point of this research, with several recent publications in the area of MEMS-based conversion.[40, 41, 42] It is interesting to note that the Lal labs and the Sun labs have recently started publishing jointly together, starting in 2008.[43] In all of these publications, however, the discussion revolves around increasing the voltage of the piezoelectric conversion system, and no reports have been given (other than theoretical calculations) of an actual power produced by these systems. Even theoretical predictions place the possible power from such devices in the nanowatt range.

(U) Future Trends in Radioisotopic Conversion

(U//~~FOUO~~) Of all the possible radioisotopic technologies, the one most likely to continue to be used will be based on thermoelectric systems. Manufacturing of these devices continues to become refined, and new technologies based on both cooling and heating will reduce the size of such devices to the point where they can become unobtrusive. Rafaelle's method of using radiophosphors seems to be the next most promising technology, but is obviously limited by the size of the source material and the eventual aging of the radiophosphor matrix under extreme dose. These devices could conceivably be improved into the low microwatt range with very low (hundreds of microcuries) sources, and could be made very difficult to detect, and can achieve sizes of perhaps 1squre centimeter and a few hundred microns thick. The energy limiting step seems to be the efficiency of the radiophosphor itself, combined with the efficiency at low "light" of the photovoltaic. If either of these systems improves their efficiency, the overall efficiency of the converter stands to gain as well. The rest of the technologies here, while perhaps interesting, are unlikely to result in a fieldable technology within the next decade, as the technological hurdles for practical application (production of steady DC current at a potential sufficient to do useful electrical work) remains limited by aging or secondary conversion issues.

(U) Ultrathin Semiconductors

(U) Introduction to Ultrathin Semiconductors

(U//~~FOUO~~) Ultrathin semiconductor devices are keys to making flexible and paper-thin electronics, and very high functional density microsystems for applications in consumer electronics, intelligence gathering and national security activities. In this section, we have analyzed the past trends, highlighted some of the leading edge ultrathin semiconductor technologies around the globe, and forecasted the state of the technology for the next 10 years. Some of the specific applications where thin semiconductors are used as radio frequency identifications (RFIDs) and tags, embedded computers and microprocessors, smart sensor modules (for example, for monitoring of bridges and buildings), climate monitoring equipment, deep-sea probers, medical implants, smart cards, thin displays, thin solar cells, portable communication and

sensing devices, wearable electronics, and space-based sensor systems. The main reasons for using thin semiconductors devices in these applications are for:

- Facilitating thin and flexible electronics like smart cards, RFID Tags and e-papers
- Getting a very high functional density in a small form factor,
- Improving heat dissipation away from the device, and
- Reducing the device parasitic losses (namely resistance, inductance and capacitance)

(U//~~FOUO~~) Semiconductor devices are made by depositi ng very thin layers of semiconductor functional circuit layers, typically ranging in thickness from sub-micrometer to 8 micrometers, on a growth or host substrates. There are two broad types of semiconducto r materials used— inorganic and organic. The most commonly used semiconductors are inorganic. Curren tly organic semiconductors are in their infancy and are being considered for low cost and low performance applications. However, that will change in the future with the development of high performing organic semiconductors. There is also a paradigm shift occurring with the new developments involving printable inorganic and organic electronics to make thin semiconductor circuits at lower cost.

(U) Inorganic Semiconductors (Silicon and Compound Semiconductors)

(U//~~FOUO~~) Currently, most commonly used devices in electronics are silicon-based. Due to the popularity of high frequency applications, III-V compound semiconductors use has also been rapidly rising in the last 10 years. The minimum thickness that can be obtained in the silicon-based devices is sub-micrometer range. This thickness is achieved by removing the host substrate completely, leaving only the device circuit layers. The majority of thin semiconductor devices are made in two process steps. First, the devices are fabricated in a semiconductor foundry using wafers of normal starting thickness. Next, these devices are thinned from the backside to get the final desired thicknesses. There are three techniques for thinning semiconductors. The most common thinning technique involves a combination of mechanical grinding/polishing and chemical etching techniques. Mechanical grinding/polishing is used to remove the bulk of host substrate material faster at low cost. However, mechanical process will leave a 10-to-30-micrometers-deep damage layer containing microcrack s, which, if not removed, will make the devices mechanically very fragile. This issue is critical for devices that are thinner than 50 micrometers. The key to getting devices thinner than 50 micrometers using mechanical techniques is to remove the damage layer by either chemical-mechanical polish and/or by chemical etching. The second technique to achieving thin semiconductors is by either dry- or wet-etching. In the recent years, some of the leading edge researchers have achieved very thin devices (less than 1 micrometer thick) by wet- or gas-phase-etching. The third technique used for semiconductor thinning involves "smart cut" process.[44] In this process, hydrogen ion layer implanted below the buried oxide layer in silicon forms a damage layer, which cleaves when the silicon wafer, is heat treated. Very thin layers of semiconductor (~ 5 micrometers thick) can be separated from its host substrate and then bonded to a different receiving wafer. Thin silicon devices or wafers, when thinned to below 30 micromet ers, show flexibility and translucency as illustrated in figure 9.[45,46] Thin semiconductor devices or wafer are very fragile below 100 micrometers thick, and they require special techniques to handle them. Semiconductor devices thinner than 50 micrometers cannot be handled as "standalone," and they have to be either supported by a rigid carrier wafer or, as demonstrated in some recent research, mixed with organics into a fine particle paste or ink, which can then be transferred or printed on to flexible substrates.[47]

(U//~~FOUO~~) Thin semiconductors are seldom used by themsel ves; they are typically integrated with other electronic devices and circuits in a product in two methods. First, thin semiconductors are interconnected with the rest of the circuitry on 2-dimensional flexible or rigid substrates. Figure 10a[48] shows example of a demonstration module containing four thin silicon devices, 30 micrometers thick, assembled on a flexible circuit board. Second, thin semiconductors are stacked vertically in 3-D to provide very high

functional density in a small form factor. Figure 10b[49] shows an eight-die stack memory module from Samsung, South Korea. In this technology, 50-micrometer-thick silicon memory devices are stacked and interconnected using copper-filled using thru-silicon vias. Figure 10c[50] shows a cross-section view of three-die stack from MIT Lincoln lab using 5 micrometer thick CMOS devices interconnected using thru-silicon-vias.

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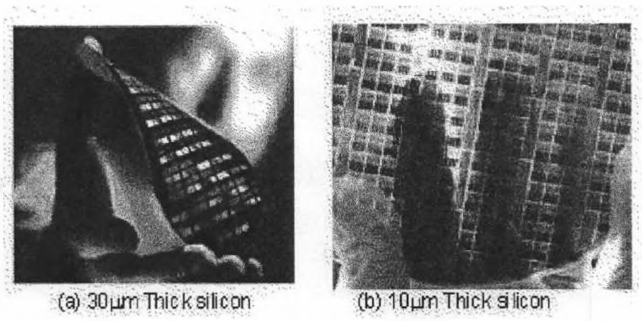

Figure 9. **(U//~~FOUO~~) Ultrathin Silicon Semiconductor Wafer (a) Showing Flexibility, (b) Showing Transluency**

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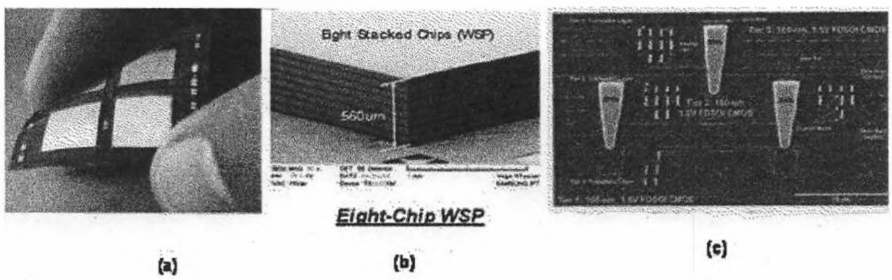

Figure 10. **(U//~~FOUO~~) Example of Thin Silicon Integrated Circuits: (a) 30 Micrometer Silicon Integrated Circuits on Flex Circuit Board [5]; (b) 8-Die Stack NAND Flash Memory Module Using 50-Micrometer-Thick Memory Devices [6]; (c) 3-Die Stack Imager Module Using 5-Micrometer-Thick CMOS Devices [7]**

(U) Organic Semiconductors

(U//~~FOUO~~) The most commonly studied organic semiconductors are transistors fabricated with Phthalocyanines and Oligoacenes.[51] The Oligoacenes and in particular Pentacene have recently attracted considerable attention because of their excellent charge transportation characteristics. Organic semiconductors are deposited on host substrate that is already thin, for example, 25- to-50-micrometer-thick polyimide. Currently, very limited circuitry can be integrated in organic semiconductors because of the performance limitations of organic transistors and diodes. However there are many new on-going research projects throughout the globe that are exploring new materials like carbon nanotube-based

semiconductors that can be inexpensively deposited as thin films on thin and flexible substrates and can function with high performance

(U//~~FOUO~~) Organic semiconductors, shown in figure 11, are inherently flexible, thin and lightweight.[52,53] They can be fabricated in large format, and they are relatively less expensive to fabricate. Since these devices are inherently flexible, a need to further thinning these devices has not been emphasized. However, if thinner devices are needed, then as-fabricated devices can be further thinned from the backside. They can be mass-produced using low cost deposition processes like printing or stamping on large sheets or using roll-to-roll technique.

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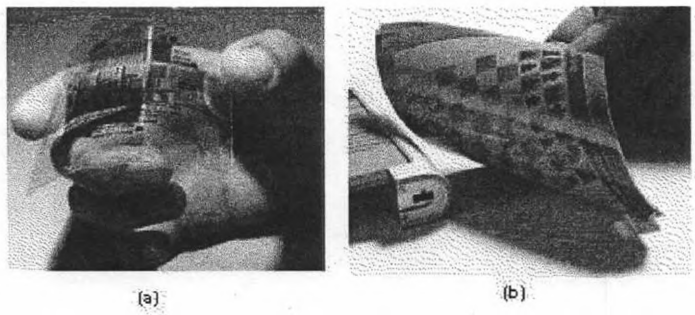

Figure 11. **(U//~~FOUO~~) Examples of Thin Organic Semiconductors: (a) Printed Semiconductors on Flexible Substrates; (b) Rollable Organic Displays**

(U) General Research and Development Trends in Thin Semiconductors

(U//~~FOUO~~) Appendix I summarizes the literature search parameters—the key phrases used and MindMap topics. Our literature search resulted in a list of publications discussing fabrication, integration and application of ultrathin semiconductors. As shown in figure 12a, the number of publications has been increasing since 1983. However due to recent economy slowdown, pace has slowed down since 2006. Figure 12b shows the contour map of the major sub-topics extracted from our survey literature. The specific end-use applications, where thin semiconductors are employed, are in smart cards, RFID tags, tracking sensors, thin displays, thin solar cells, medical implants, wearable electronics, portable electronics, high-end computers, space- and defense-related sensors and systems, high-end and low-end consumer electronics, and LED lighting panels.

(U//~~FOUO~~) Our survey has shown that thin semiconductors are needed in many applications because they enable:

- Thinner, flexible electronics
- Higher functional density electronic circuits (thin devices can be stacked in 3-D to provide a very high functional density in small volumes)
- Lower Cost electronics (mostly enabled by thin organic semiconductors, which can be fabricated at low cost on large panels or rolls)

(U//~~FOUO~~) The major sub topics breakdown of these publications can be broadly categorized into three main technology application groups, which are:

- Thin, flexible circuits
- 3D IC-stacking or packaging
- Thin solar cells

(U//~~FOUO~~) The yearly publication trends in each of these technology groups are plotted in figure 13. The use of thin semiconductors in thin flexible electronics dominates over 3-D electronics and thin solar cells. Publications relating to thin, flexible electronics have been flourishing since 1980. Many sensitive applications like RFID tags, smart cards, and "concealed" electronics will fall into this category. The publications relating to 3-D electronic technologies started in 1995, and they are increasing at a rapid rate since then. Three-dimensional technology could be used in applications where high functional density in a small form factor is required, for example, image analysis and advanced space-based sensors, high-end personal digital assistants and "concealed" electronics. Since thin solar cells are relatively small user of thin semiconductors, they are not discussed in more detail in this report.

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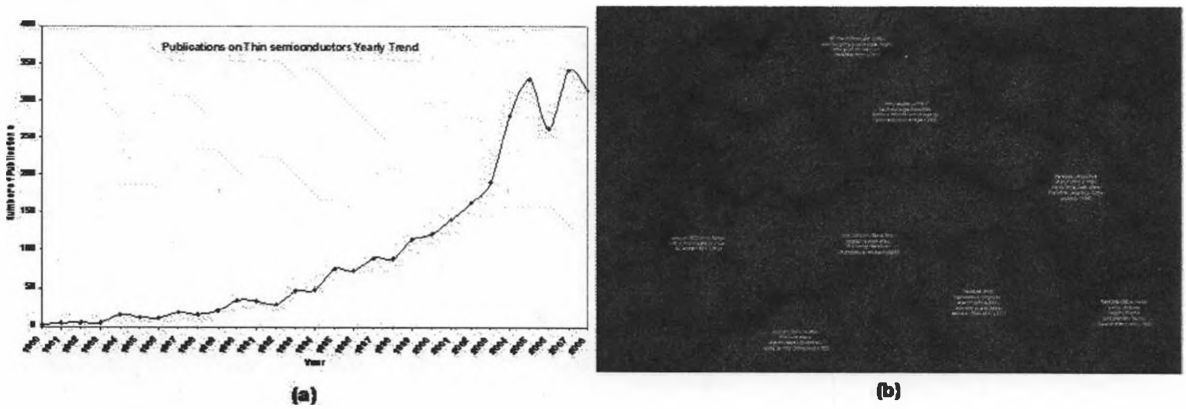

Figure 12. **(U//~~FOUO~~) The Yearly Trend from 1980 to 2009 of the Total Publications with Reverence to Thin Semiconductors (a); The Contour Maps of the Main Thrust Areas in Reference to Thin Semiconductors**

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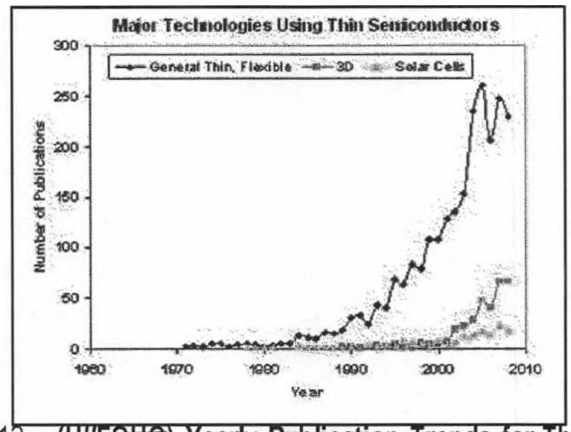

Figure 13. (U//~~FOUO~~) Yearly Publication Trends for Three Major Application Technology Groups That Use Thin Semiconductors

(U//~~FOUO~~) Some of the relevant sub-topics relating to thin semiconductors discussed in the literature are the following:

(U//~~FOUO~~) **Thinning processes**: Although the majority of these publications report the use of thin semiconductors, only a very few of them discuss the detail processes for thinning. Three techniques that have been reported are mechanical grinding, lapping and polishing, chemical etching (dry and wet etching), and "smart cut" process.

(U//~~FOUO~~) **Integration of thin semiconductors**: The majority of the literature surveyed discussed integration of thin semiconductors on thin, flexible substrates or in 3-D electronics. There are many variations of these integration technologies being developed depending on the end-use applications.

(U//~~FOUO~~) **Thin, flexible organic semiconductors**: Currently used organic semiconductors are limited to very simple devices as used in displays and LED lights. Even in these applications, the reliability and performance of these devices are marginal. Thus, there is on-going research to make these devices more complex, more economical and more integrable in large format (for example, roll-to-roll processes). Some of the new research involves integrating carbon nanotubes and sub-micrometer sized silicon devices into organic-based inks and pastes, which can be printed or stamped on flexible plastic boards.

(U) Country Trends in Thin Semiconductors

(U//~~FOUO~~) The breakdown of the publications that were published since 1980 by authors in various countries is shown in figure 14a. In the data reported, the countries represent the authors from the countries. Publications prepared with collaboration by authors from different countries have been counted in the statistics of each of the participating countries. As seen in the figure, the United States' lead is very significant, followed by that of Japan, Western European countries, and South-East Asian countries. This trend indicates the discretionary research and development funding available in these countries to do leading edge work to make electronics thinner, more flexible, and with high functional density. One main reason for European and Asian countries' interest in thin semiconductors is that the consumer electronics is going "thin." However, the technologies used in thin consumer products can be very effectively used in sensitive applications, for example, covert information gathering. It is also noteworthy that publication

out of the United States is more than of three times that of any other country; however, if regional comparisons are made, for example, European and Pacific Rim Region, then the publications from these regions are on par with or higher than the United States. This trend implies that the individuals or countries wanting to develop thin, flexible, or high-density electronics using thin semiconductors have a choice, and they probably will not have to travel far from their host country to obtain them.

(U//~~FOUO~~) Figure 14b shows the yearly trend for the major publishing countries. The United States has historically led the research and development activities in thin semiconductors. Outside of the United States, Japan is leading the research and development activities. Surprisingly, Germany, France, China, Taiwan, and South Korea have picked up the pace in the technology in recent years in spite of starting late, and they are presently on par with Japan. The number of publications coming out of these non-US countries is small fraction of that of US publications; however, their quality and completeness of work are on par with or in some cases better than that of the United States, particularly with the Japanese publications. In our opinion, based on the technical content of the publications, Japan is on par with or maybe better in some cases than the United States in developing thin semiconductors and thin electronics. Western European countries, specifically Germany and France, are also not much behind the United States, specifically in newer technologies relating to 3-D electronics, RFID tags and smart cards.

(U//~~FOUO~~) We also surveyed the data to see the strengths of each of the top publishing countries. The United States led in all application categories. Japan, like the United States, was strong in all application categories. Germany and France are strong in 3-D, smart cards, and RFID tag development. China, Taiwan, Hong Kong, and Singapore have a small presence in all technologies, but are not dominant in any one of them.

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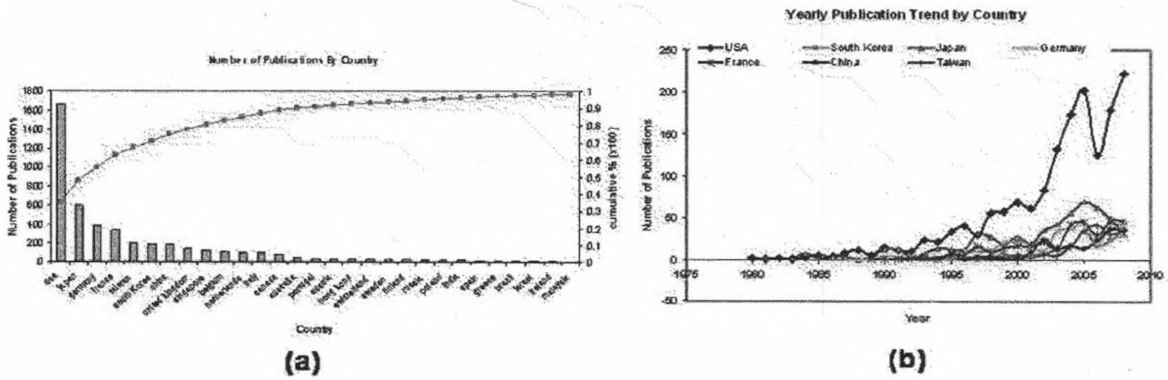

Figure 14. **(U//~~FOUO~~) Number of Publications from Individual Countries (a); Yearly Publication Trend of Publications from United States, South Korea, Japan, Germany, France, China, and Taiwan (b)**

(U//~~FOUO~~) The research and development activities in the United States relating to thin semiconductors surpass that of all other countries. Since the main focus of this report is on non-US research and development activities, we will highlight only two US reports that could impact the future. In 2008, Prof. Ma and his team[54] at the University of Wisconsin reported that they can fabricate 0.25-micrometer- thick silicon thin-film transistor, which can then be transferred to a thin, flexible plastic substrate, and they have built a circuit operating at a speed of 7.8 GHz. This work has demonstrated a potential of developing a very thin communication circuit. In 2005, J. Rogers, E. Menard and R. Nuzzo[55] of the University of Illinois, demonstrated a bendable single crystal silicon, ~0.1 micrometer thick, on flexible epoxy substrates. The device was separated from its growth substrate by high frequency etching and then

transferred to epoxy substrate using a printing technique very similar to stamping. This work is a leading edge demonstration of manufacturing ultrathin electronic circuit, which can be integrated on a substrate at a low cost.

(U//~~FOUO~~) In Germany, researchers at Infineon technologies, C. Lauterbach, W. Weber and R. Glaeser[56] have published the basic concept of integrating thin electronics in fabric and have proposed to fabricate "smart textile" based on a wired peer-to-peer network of microcontrollers with integrated sensors or actuators.

(U//~~FOUO~~) From 2000 to 2009, the researchers at IZM Fraunhofer in Berlin and at Munich, Germany[57,58,59] are actively developing techniques for fabricating thin semiconductors that can be used in thin flexible RFID tags, smart cards, and 3-D microsystems. They have demonstrated thinning of semiconductors to less than 10 micrometers using a low cost and more-widely applicable thinning technique involving a combination of mechanical grinding/polishing, and etching. Some of the leading researchers are H. Reichl, R. Weiland, K. Bock, M. Feil, A. Klumpp, M. Toepper, C. Landesberger, R. Aschenbrenner and P. Ramm. These researchers work with small and large companies like Infineon technologies AG to bring the technologies to market.

(U//~~FOUO~~) In France, Andre Auberton-Herve and Jean-Michel Lamure from CEA-Leti,[44] and later from SOITEC, developed the "Smart Cut" process in 1992 to fabricate silicon-on-insulator wafers, which is widely used in IC fabrication today. This same technology is also used in thinning semiconductors to less than 5 micrometers. Thin semiconductors can then be mounted on other materials to optimize the circuit performance. For example in 2003, Researchers at CEA-Leti[60] reported combining silicon germanium (SiGe) and indium phosphide InP semiconductors to silicon, and silicon ICs on more thermal conducting materials like silicon carbide (SiC).

(U//~~FOUO~~) In 2008, K. de Munck, P. de Moor, B. Swinnen, and C.V. Hoof[61] of IMEC, Belgium reported the effect of ultrathinning semiconductors on its physical and electrical performance. Mechanical thinning processes could leave 24-micrometers-deep damage layer on the surface. This mechanically damaged layer will make thinned semiconductor to crack easily; thus, a special attention is given to removing the damage layer, whenever semiconductors are thinned mechanically. This Belgian group also reported that this damage layer did not degrade the electrical performance of semiconductors thinned down to 5 micrometers. In another research activity from Belgium in 2007, E. Beyne and F. Iker[62] of IMEC have reported an alternate way to integrate thin semiconductors in 3-D. They have embedded 15 micrometers thick dies in 3-D stack in thin multi-layers of polymer dielectric, benzocyclobutene (BCB). This technology is potentially interesting for many security applications where electronics have to be "concealed."

(U//~~FOUO~~) In 2007, L. Wang, T. Zoumpoulidis, M. Bartek, K. Jansen, L. J. Ernst and G. Zhang[63] of the Netherlands have developed a thin, flexible integrated electronic technology, called CIRCONFLEX for RFID tags and "smart" skin. In health-related applications, thin flexible electronics is particularly important as sensor modules that can be worn as skins or implanted inside the body.

(U//~~FOUO~~) In 2005, S. Shiraishi, T. Takenobu, Y. Iwasa, T. Iwai, H. Kataura and M. Ata of Osaka University in Japan[64] reported a successful fabrication of single-walled carbon nanotube field effect transistors. After this report was published, several groups[65] around the globe reported the synthesis and integration of thin-film carbon nanotube transistors by printing and showing mobility of as high as 100 cm^2Vs^{-1}. Carbon nanotubes have a theoretical potential of having mobilities of 10,000 cm^2Vs^{-1}. This work is significant because nanotube transistors can potentially have a superior performance unlike other organic transistors as well as can also be deposited as thin film on a substrate using low-cost printing techniques.

(U//~~FOUO~~) In another development, in 2007 the leading researchers, Sano et al,[66] from Osaka University in Japan were able to fabricate thin silicon-on-insulator (SOI) wafers with 0.1 micrometer thickness and

uniformity of 0.01 micrometer by using numerically controlled plasma chemical vaporization machining (PCVM) technique, which involves gas-phase etching. This is one of the thinnest semiconductor device ever fabricated using an etching technique.

(U//~~FOUO~~) In the first of the other two noteworthy research reports, H. Shinohara et al,[67] from Kyoto University were able to thin a silicon IC to 1 micrometer thickness after bonding the front side of silicon to SiC. In the second report, S. Inoue et al of Seiko Epson[68] has developed a technique, called Surface Free Technology by Laser Annealing (SUFTLA) to thin poly silicon thin-film transistor circuits from the original glass or quartz host substrates and transferred it to plastic substrate for applications in paper-thin smart displays and microprocessors.

(U//~~FOUO~~) For the most part, Chinese researchers are following the lead of US, European, and Japanese developers. Many Chinese publications are focused on thinning silicon, Gallium arsenide (GaAs) and germanium by smart cut technology. In 2007, Y-L Guo, J. Zhou, S-Y Zhu and Y-P Huang of Fudan University, Shanghai[26] reported their work on investigating proton (H+) implantation in GaAs for smart cut process to thin it and then subsequently bonding GaAs to silicon substrate. In 2003, C. Z. Gu et. al of Chinese Academy of Sciences in Beijing[69] reported on their work on depositing thin silicon layers on diamond films, which has superior thermal conductivity and radiation properties.

(U//~~FOUO~~) Researchers in Taiwan are doing some leading edge development of thin electronics. In 2006, C.-T Ko et. al of ITRI in Taiwan[70] reported a chip-in-substrate package (CiSP) technology. In this technology, 50-micrometer-thick memory devices were embedded in dielectric layers. This technology is also one of the few technologies around the world being developed that could be also be used as concealed electronics. In 2008, W.-C Kao et al of National Taiwan University[71] reported a development of smart card with flexible electrophoretic display and one-time password generating electronics.

(U//~~FOUO~~) Samsung in South Korea announced in 2006 the first product using 3D IC stacking technology which integrates thin semiconductor wafers in 3D. However, the researchers at Samsung have not published any detailed technical papers describing their technology, except for a photograph of their product.[72]

(U) International Interactions in Thin Semiconductors

(U//~~FOUO~~) Figure 15 shows the network of interconnection between researchers from different countries. The data indicates that a majority of the publications involve US authors, but also a large number of research reports are also coming from the world and the network among them is extensive. Much of this network is established naturally through the training of graduate students and post doctoral students who move on establish their own programs at other locations, often returning to their home country after study abroad. This may be the reason for US publications tending to be more international, since US is more popular for graduate studies for international students. The analysis also highlights that European countries tend to collaborate among themselves more frequently, and some of these recent inter-European collaborations may be attributed to the formation of European Union in 1993.

(U//~~FOUO~~) On examining the network of collaboration in figure 15 in detail, we found that several of these interactions were not relevant to this report. For example, in Japan most of the interactive research involved more basic fundamental research at universities involving thin-film layers of semiconductor devices, and only about five interactive publications were relevant. This was also true about interactive reports from other minor countries like Algeria, Jordan, Saudi Arabia, and Iran.

(U//~~FOUO~~) From 2000 to 2009, J-Q Lu, R.J. Gutmann and Y. Kwon of RPI in the United States published extensively on thin semiconductors in reference to using them in 3-D IC-stacking technology.[73,74] One of the co-authors, Y. Kwon, also has a joint appointment at Rennsselaer Polytechnic Institute in the United States and Inha technical College in South Korea. One of their co-authors, J. Seok,

later joined Samsung Electric Co. in South Korea. As mentioned in the earlier section, Samsung was the first semiconductor company to announce a product using 3-D IC stacking technology.

(U//~~FOUO~~) In 1990s, Q-Y Tong and U Goesele did some pioneering work together on 3-D IC-stacking that also involved bonding of carrier wafers for thinning of semiconductors.[75] Q-Y Tong had affiliation with Microelectronic Center, Southeast University, and Nanjing Institute of Technology in China, Duke University in the United States, and Max-Planck Institute in Germany .[75,76,77] U. Goesele had affiliation with Duke University and Max-Planck Institute.[75,77] Q-Y Tong has published jointly with authors from China, Germany, and the United States. U. Goesele has published jointly with authors from the United States and Germany.

(U//~~FOUO~~) In 2008, Christiaens and Vanfleteren from Belgium and Loeher and Pahl from Germany[78] collaborated to develop a thin integrated electronics technology by embedding ultrathin chips, greater than 15 micrometers thick, in flex circuit boards or between thin layers of spin-on polyimide films.

(U//~~FOUO~~) In 2007, I. Sayhan and T. Becker from Germany, E. Abad and S. Marco from Spain, and S. Zampolli , A. Scorzononi, B. Mazzolai and I. Elmi from Italy[79] reported developing a thin flexible tag microlab for food monitoring. This tag combines physical and chemical sensors with RFID communication capabilities.

(U//~~FOUO~~) Traditionally, IZM Fraunhofer has limited its collaboration to other European countries; however, recently it has joined an advanced packaging consortia led by Rao Tummala at Georgia Tech to develop advanced 3-D integration technologies that uses thin semiconductors. No publications have yet come out of this collaboration.

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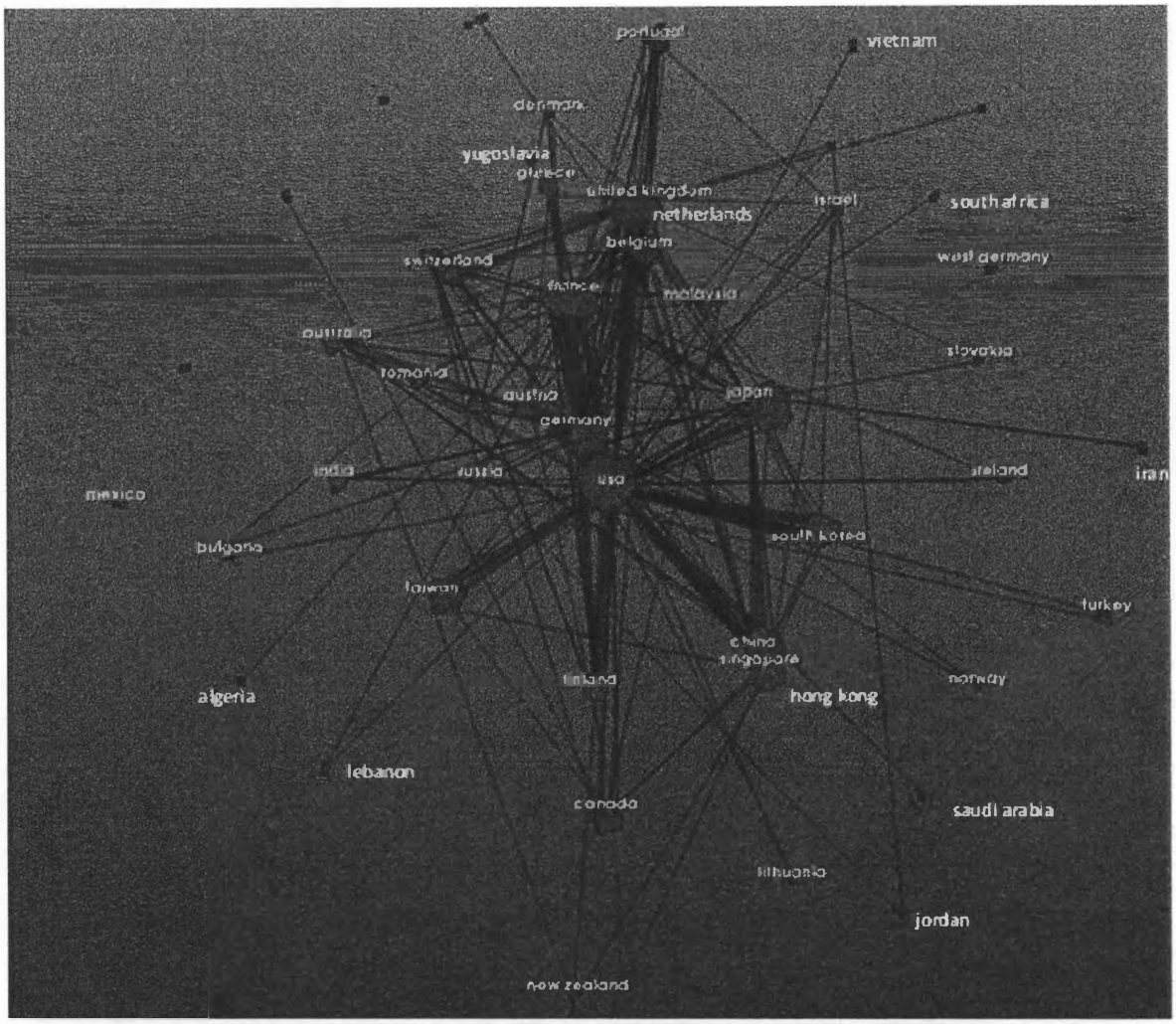

Figure 15. **(U//~~FOUO~~) Map Showing Collaboration Between the Authors in Various Countries, Each Line Representing a Collaborative Publication (The Red Area Qualitatively Indicates the Number of Publications in the Country)**

(U//~~FOUO~~) In 2007 another collaborative research publication from Europe, I. French, of Great Britain, F. Templier of France, and H. Lifka of the Netherlands [80] collaborated to develop a thin, flexible display panel using Electronics on Plastic by Laser Release (EPLAR) process. This display involves thin-film transistors array with driving circuitry is deposited on thin poyimide layer. This process was developed by Phillips in the Netherlands and will be manufactured by PVI in Taiwan.

(U//~~FOUO~~) In 2007, S. Pozder et. al at Freescale in the United States collaborated with CEA-Leti researchers, M. Fayolle et. al, and G. Paasemard of ST Microelectronics in France [81] to develop a two-wafer 3-D stack, which used less-than-10 micrometer- thick silicon semiconductor wafers. The researchers from Freescale [82] have also collaborated separately on 3-D interconnects with G. Hillman of Datacon and G. Pargfrieder of EVG, both in Austria. Both these companies are equipment suppliers,

Datacon specializing RFID assembly equipment, and EVG makeing equipment used in 3-D IC-stacking technologies.

(U//~~FOUO~~) In 2007, A. Schindler, J. Brill, and N. Fruehaf of University of Stuttgart in Germany [83] collaborated with J. P. Novak and Z. Yaniv, Applied Nanotech in the United States to develop processes for carbon nanotube transistors on plastic foils to make thin displays.

(U//~~FOUO~~) In 2009, T. Takenobu of Tohoku University and M. Shiraishi of Osaka University collaborated with Sheng-Yi Lu of National Tsing-Hua University in Taiwan [84] to develop ink-jet printing process for carbon nanotube thin-film transistors on flexible plastic substrates. Their study has realized high on-off current ratio ($\sim 10^{4}$) and high mobility (0.4 $cm^2/(V.s)$). This collaboration is noteworthy because it has brought together the leading researchers from Japan and Taiwan.

(U) Future Trends in Thin Semiconductors

(U//~~FOUO~~) In the next five years, thin semiconductors will be increasingly used in thin and flexible electronics, and in high functional density 3-D electronics. In the future beyond five years, semiconductors can be integrated in high density electronics that are also thin and flexible. These technologies will enable today's products that are much thinner and smarter and bring to the market new products that will only be limited by our creativity.

(U//~~FOUO~~) In next five years, products with thin semiconductors will be everywhere around us—for example, in personal digital assistants with built-in computers and pico-projectors, e-paper that will replace today's newspaper, large-format e-displays, bio-implants to monitor personal health, more complex RFID Tags that will be constantly monitoring the ambient environment, smart-cards that will replace paper-money and wearable electronics and smart skins. Thin semiconductors will also enable many new creative products, such as thin displays that will make smaller appliances invisible with the image displays from the background.

(U//~~FOUO~~) Thin semiconductors with thickness of less than 10 micrometers will be routinely fabricated and integrated into everyday consumer products. Thin semiconductors of thickness less than 5 micrometers will also be used in high-end products. Semiconductors devices with less than 1 micrometer will become a reality, and they will be demonstrated in more prototype applications. The maturation of ultrathin semiconductor technologies will enable a new paradigm shift towards printed inorganic and/or organic semiconductors. Printed electronics will allow very large-size substrates to be processed at a significantly lower cost as panels or on flexible films using reel-to-reel technique. With the printed inorganic and organic electronics technologies, the large initial capital expenditures of greater than $3 billion to build IC factories will no longer be needed, and this reality will significantly alter the business, marketing, and geography of semiconductor production. More countries will be able to build relatively less expensive factories to mass produce thin, flexible electronics for use in applications needing simpler circuits and lower cost.

(U//~~FOUO~~) Currently, the printed electronics do not meet the performance and complex circuit requirements of many high-end applications. During the next five years, there will be continued efforts to improve the performance by using newer class of printable materials like carbon nanotubes and printable inks made of silicon nanocrystalline particles.

(U//~~FOUO~~) With the new paradigm shift, processes for thinning and integration of thin semiconductors will also continue to undergo a technology split between two broad categories:

(U//~~FOUO~~) **Back-End-of-the-Line thinning of inorganic semiconductors:** Mechanical grinding/polishing and chemical etching will be the major process technique to thin silicon and compound semiconductors less than 10 micrometers thick. Smart Cut process will become more common in manufacturing the devices less than 5 micrometers thick. Dry or wet etching techniques will be the dominant technique for semiconductor devices less than 1 micrometer thick.

(U//~~FOUO~~) **Printed inorganic and organic electronics:** In the printed inorganic semiconductors process flow, the first step is to fabricate very thin (less than 1 micrometer thick) inorganic semiconductor particles by dry and wet etching, which can then be dispersed into a slurry or paste for printing. Organic semiconductor printable inks will also continue to see a significant growth.

(U//~~FOUO~~) A wide variety of integration techniques will be used in the next five years. For applications requiring thin flexible electronics, thinner silicon and compound semiconductors will continue to be assembled either on organic film or sandwiched between two film layers. For high-end applications, thin devices (less than 10 micrometers) will continue to be integrated in 3-D with other devices or with better heat sink materials like diamond, SiC or copper. Printed organic and inorganic electronics will make the fabrication of semiconductors and their assembly into products much simpler and cheaper. Stamping and screen printing for coarser resolution and ink-jet printing for finer resolution (~ 1 micrometer) will be the major patterning techniques used.

(U//~~FOUO~~) In the United States, leading edge research and development will continue, but the US lead in manufacturing will reduce even further. The major upcoming countries will be Germany, Belgium, China, Taiwan, Japan, and South Korea. Many smaller countries in all continents will seriously explore the possibilities for establishing printed electronic industries because of smaller capital investment needed for this technology.

(U//~~FOUO~~) Thermal management and cost issues will play a major role in the future technologies using thin semiconductors.

(U//~~FOUO~~) In the next 10 years, thin semiconductors will be used in most consumer and high-end applications. Thin semiconductors will increasingly enable our lives to be interwoven with information about our environment. Thin silicon and compound semiconductors thinned to less than 1 micrometer will be more commonly used in electronics. These devices will enable thin flexible electronics with higher functionality and miniaturization. Printed electronics will no longer be confined for low-end applications. Printed organic and inorganic electronic performance and functionality will significantly improve to yield very high performance at low fabrication costs. The key to this revolution will be the new materials like carbon nanotubes and nanocrystalline silicon.

(U//~~FOUO~~) In applying the future electronics in products, creativity rather than the technology will be a limiting factor. However, the main issues that still have to be dealt with will be thermal management, disposal of throw-away electronics, and raw material cost, and supplies. The trend to flourish thin semiconductor internationally will continue at a faster pace. Even smaller countries from all continents will have established printed electronic industry. However, the high-end products still be produced in the United States, Japan, Germany, China, Belgium, China, Taiwan, South Korea, Singapore, and maybe India.

(U) Conclusions and Summarizing Remarks

(U//~~FOUO~~) From the individual point forecast studies reported above, we can make several high-level conclusions. The first is obvious, and adds to the increasing din of the same complaint across several areas of engineering and scientific endeavor: the United States is losing, and in some areas has lost, the technological lead for developing new technologies in small energy storage. However, battery technology will continue to be the predominant energy storage technology for the next five years, mostly due to the advances in lithium ion technology. It is an expectation that the energy density of the current best batteries will be increased by perhaps 20 percent just based on improved materials, with no gains from packaging. For thin and flexible batteries in particular, enhancements in packaging and sealing will likely dramatically improve the energy density of these systems and probably make them practical at the 200-to-400-micrometer-thick level to power e-paper, flexible displays, and other low power devices. Thinning below this level is unlikely because there is no commercial driver to become thinner; thinner than this is

strictly the purview of military applications (because of the loss in capacity it represents). Printing as a manufacturing technology for disposable "green" batteries will become predominant, and lead a disposable electronics change (like displays built into the cardboard box of a cereal box, that is discarded when the box is empty). Battery life will be short lived, but the expectation will be for one to two weeks of low power operation for these devices.

(U//~~FOUO~~) Supercapcitors are already dominated by Chinese research. The research is deep, wide, and covering all bases. Significant benefits from this investment are likely, and it is within the realm of possibility that a Chinese-made supercapacitor with an energy density of 300 to 500 watts per kilogram will emerge into the practical market. Since the Chinese have stated this is for military and space applications, it is likely that supercapacitor based technologies and power sources may already be in the field for niche applications.

(U//~~FOUO~~) Mechanical and radioisotopic power sources are unlikely to make significant strides towards applicability in the next five years, simply because of the low energy densities of the systems. It is very unlikely that such systems will beat current battery energy densities, let alone predicted values in five years. However, mechanical systems that represent one shot, high impulse energy discharges (like PZT "shock-strike" actuators capable of delivering mA of current for tens of milliseconds driven by a CNT prestressed fiber bundle) may become reality in military applications for single burst transmission energy from distributed sensor systems. Radioisotopic systems with small scale thermoelectric (TE) systems may find field application at the 1-2 curie source level, but all the direct conversion systems are currently too low in efficiency and too sparsely investigated to make real progress.

(U//~~FOUO~~) Ultrathin semiconductors will quickly leave the research and development realm and enter productization in the next five years. What was once the exclusive realm of military technology to thin active devices to 5 microns is now a commodity market, and e-paper, implants, and wearable electronics will drive this further. CNT gate technology may gain market acceptance for niche applications with early (expensive) products with high unit utility. Printed organic semiconductors will become a reality, and most of the current low end chip based market will be replaced by printed electronics within the next five years. Unfortunately, the maturing of the technology will lead to an inevitable shift of manufacturing base away from the United States, and the current US dominance in the ultrathin semiconductor market will fade as the Pacific Rim and European competitors take over the majority of this market.

(U) Acronyms and Abbreviations

$\mu Ah/cm^2$	microampere per square centimeter
$\mu Ah/cm^2$-μm	microampere per square centimeter per micrometer
μm micrometer	
BCB	benzocyclobutene
CiSP	chip-in-substrate package
cm^2Vs^{-1}	square centimeters per statvolt per second
COTS	commercial-off-the-shelf
CrN	chromium nitride
DBP	dibutylphthalate
EPLAR	Electronics on Plastic by Laser Release
GaAs	gallium arsenide
GeOx	germanium oxide
IC integrated	circuit
InP	indium phosphide
IPS	infinite Power Solutions
$Li/Li_4Ti_5O_{12}$	lithium/lithium titanate
$Li/LiPON/Ag_{0.5}V_2O_5$	lithium/lithium phosphorus oxynitride/silver vanadium oxide
$Li/LiPON/CuWO_4$	lithium/lithium phosphorus oxynitride/copper tungstate
Li_3MnNiO_4	lithium Manganese nitride
Li_3PO_4/Li_4SiO_4	lithium phosphate/Lithium Sulfate
$Li_4Ti_5O_{12}$	lithium titanate
Li-Al-Ti-P-O	lithium-aluminum-titanium-phosph orus- oxygen
$LiB(C_2O_4)_2$	lithium bis-oxalato borate
LiBOB	lithium bis-oxalato borate
$LiCo_{0.8}(Ni.Zr)_{0.2}O_2$	lithium Cobaltate with nickel and zirconia
$LiCoO_2$	lithium bis-oxalato borate

$LiFe_2O_3$	lithium iron oxide, lithium ferrite
$LiFeF_3$, LiI, LiF	lithium cobalt oxide
$LiFePO_4$	lithium iron phosphate
LiI	lithium halides
$LiMn_2O_4$	lithium iron phosphate
$LiMnO_2$, lithium	manganate
$LiPO_4$ lithium	phosphate
LiPON	lithium phosphorus oxynitride
$(Li_x,La_{1-3x})TaO_3$	lithium-lantanum tantalate
LSA	Latent Semantic Analysis
mAh/cm^2	milliampere-hour per square centimeter
mAh/g	milliampere-hour per gram
MEMS	Micro Electo Mechanical Systems
MIT	Massachusetts Institute of Technology
mm millimeter	
MnO_2 manganese	dioxide
nm nanometer	
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
PVCM	plasma chemical vaporization machining
PVDF	poly(vinyldiene fluoride)
RFID	Radio Frequency Identification
SiC	silicon carbide
SiGe	silicon Germanium
SiO_2	silica. silicon dioxide
SiOx	silicon oxide
SnO/SnO	tin oxide/tin oxide
SnO_2/Li	silicon dioxide/lithium
SnOx	tin oxide

SOI	Silicon-On-Insulator
SUFTLA	Surface Free Technology by Laser Annealing
TFLB	thin-film lithium batteries
TiS_2 titamium	sulfide
VO_2 vanadium	oxide
Zn-MnO_2	zinc-manganese oxide

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