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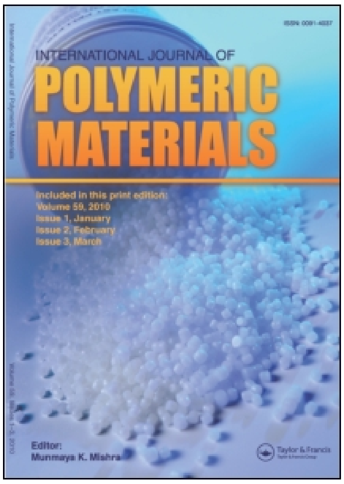

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Blue Ribbon Abstracts

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Blue Ribbon Abstracts

[NZP]: A NEW FAMILY OF REAL MATERIALS FOR LOW THERMAL EXPANSION APPLICATIONS

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Materials science is often concerned with composition-structure-property relationships. In the last four decades, dramatic advances and discovery of new materials have demonstrated how far our understanding of materials science and engineering has taken us in the fields as diverse as compound semiconductors, and composite electromechanical transducers, and the recent progress in ceramic superconductors. These scientific developments not only have made great impact on technology but also have benefited the society tremendously. The present work too pertains to one such new development in the area of low thermal expansion ceramics. It was pure innovation and serendipity which led to the development of an entirely new family of low thermal expansion materials, now popularly known as [NZP]. In the materials research and ceramic industry the importance of low thermal expansion materials is manifested in their widespread use in high anti-thermal shock applications, electronic devices, automobile industry (exhaust system components), and space and telescope technology, to name just a few.

For several decades prior to World War II the ceramic community utilized only three families of low thermal expansion materials, namely, cordierite, zircon, and silica glass. In 1948, Hummel discovered

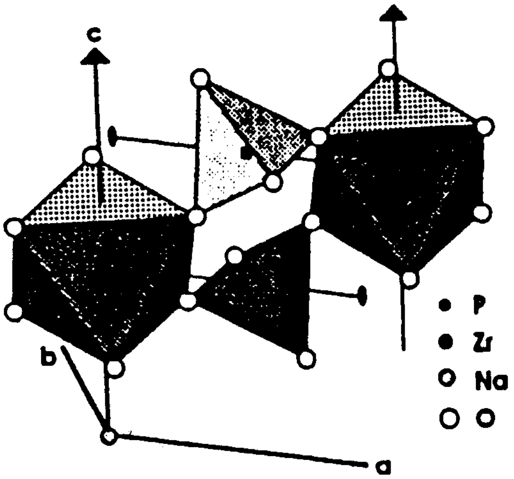

FIGURE 1 [NZP] Crystal structure.

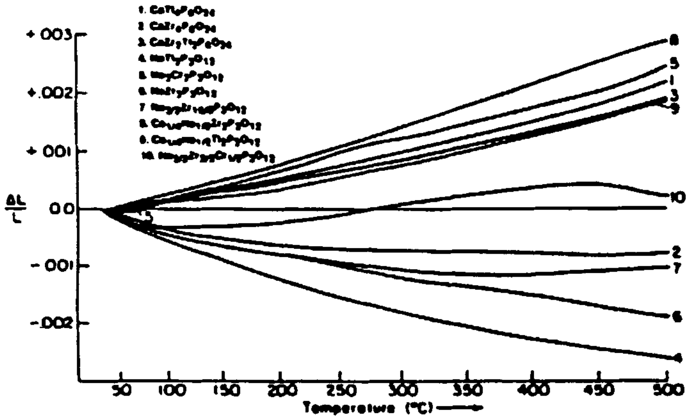

FIGURE 2 Thermal expansion of [NZP]-family.

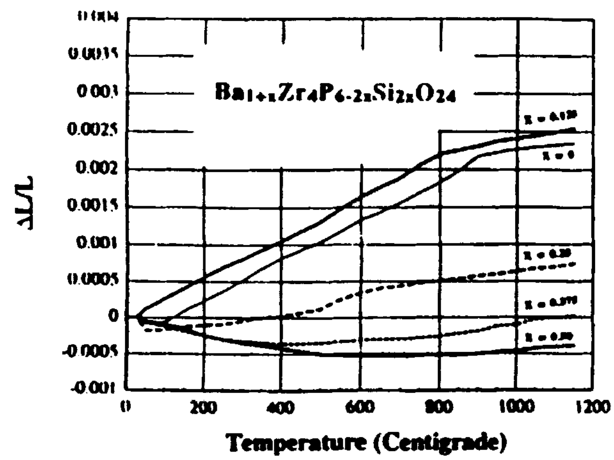

FIGURE 3 Thermal expansion of $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$.

a family of lithium aluminum silicates (LAS) which had very low and even negative thermal expansion. For nearly the next forty years this one family dominated the science and technology of low expanding ceramics. In the early 1980's, while searching for new low expansion materials for telescope mirror blanks, we by chance developed this new [NZP] family of materials, and since then tremendous amount of research has been conducted on these materials at Penn State and other institutes. This research has demonstrated the versatile utility and tremendous potential of [NZP] materials for wide ranging applications. And if the potential of [NZP] is fully exploited it would meet the ever growing demands of the modern technology, and also benefit the society at large.

[NZP] family, which gets its name after the prototype composition, $NaZr_2P_3O_{12}$ consists of a very large number of compositions which are characterized for their low thermal expansion and controlled lattice thermal expansion anisotropy, e.g. $Ca_{1-x}Sr_xZr_4P_6O_{24}$ and $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ crystalline solution series exhibit near zero bulk CTE and low anisotropy in their lattice thermal expansions. Recently, [NZP]'s have been attracting world wide attention for various diverse applications such as exhaust components in automobiles, mirror blanks for optical telescope, substrates material for electronic packaging, sulfur-batteries, nuclear waste immobilization, port-liners for diesel engines, braze-fixtures for air-craft engine, and several other potential applications. Most of these applications are attributed to the unusual characteristics of the NZP structure, such as ultra low thermal expansion, fast ionic conductivity, high thermal and chemical stability, and flexibility towards ionic substitutions. NZP crystal structure has a three-dimensional skeletal network of PO_4 tetrahedra sharing corners with ZrO_6 octahedra (Figure 1). This polyhedral network is so articulated that several large structural holes are created in the structure. These structural holes are partially or fully (depending upon the composition) are occupied by Na or Ca or another substituent ion(s), and also provide flexibility towards ionic substitution. For example Na can be replaced by H, K, Li, Cs, Mg, Ca, Sr, Ba and Cu; Zr by Ti, Ge, Cr, Al, Fe, Hf, Th, Sn, and rare earths; and P by Si, and S. This anomalous compositional flexibility is demonstrated by the fact that H, Li and Cs can exist at the same crystallographic site, a condition not known in any other structure. Partial as well as complete ionic substitutions are possible, which enables one to tailor a desired property by modifying the composition. For example, in the $Ca_{1-x}Sr_xZr_4P_6O_{24}$ and $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ systems, compositions of zero thermal expansion in certain temperature ranges have been produced (Figures 2 and 3). The low expansion behavior of these materials can be attributed, *in general, to i) strongly bonded 3-dimensional network structure ii) existence of structural holes which* may absorb some of the thermal vibrations, and iii) anisotropy in the thermal expansion of the lattice.

REAL NZP APPLICATIONS

Couple of years ago one of our students, started a company named LoTEC, Inc. which specializes in marketing, commercializing and manufacturing of the ceramics based on [NZP] structural family for various *real* applications. At present [NZP] materials are being used or tested for the following applications:

- Port-liner for diesel engines
- High temperature nozzles
- Components for Optical benches
- Braze Fixtures for air-craft engine repair and manufacture
- Components for primary metals and heat-treating industry
- Substrates for electronic packaging

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RIGIDIZED STRUCTURAL CERAMIC REFRACTORY INSULATION
RSI 900 and RSI 2200

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In the 1960's when Robert Beasley first suggested a more efficient Thermal Protection System, (TPS), for space-craft, it was not accepted as a possibility by many in his field.

Space vehicles were reusable but their heavy heat shields, ablated by charring during reentry and replacement, could be done only at great cost.

He persisted with his concept and developed the use of filament-wound pure amorphous silica fibers for radome heat shields and other high temperature uses. At this time, on staff at Lockheed Missiles and Space Company at Sunnyvale, California, he also developed Lock-Heat which was a forerunner of the present material.

By the time the concept of the space shuttle was introduced, LI 1500 had been developed. It was finally selected as the main TPS for the orbiter.

The body of the orbiter is of aluminum alloys and cannot stand up to the rigors of launch and reentry. It's TPS had to meet several stringent requirements, some of which were:

- withstand acoustical vibration and rapid decompression at launch and rapid compression at re-entry for 100 cycles;
- withstand temperatures of up to 2500°F and still maintain its dimensional stability;
- withstand the conditions of space, solar heat, extreme cold and total vacuum;
- get rid of moisture and air without fracture during launch and re-entry;
- be waterproof to cope with earth's weather conditions;
- be ultra-lightweight to add to payload capabilities, (hence LI 900).

The final form of TPS LI 900 is an open skeletal intersticed construction of fibers bonded with pure colloidal silica. This is formed into blocks, and then tiles by use of computerized machining. They are then bonded to a felt by RTV which in turn is bonded to the orbiter body. A minute space is left between each tile to allow for expansion of the aluminum body and its vibrations.

A coating for the tiles was developed by Robert Beasley which reflects solar radiation from the orbiter top to ensure shirtsleeve weather inside and re-radiates heat from friction upon re-entry. He also developed a coating for the bottom to re-radiate the higher heat of re-entry. This was later changed by NASA-Ames and patented by them.

He also developed LI 2200, a more brittle, harder material, used on some of the close-out edges of the orbiter which was altered slightly by NASA and patented.

Military applications include satellite covers and supersonic radomes. Potential domestic products include heat-cycling engines and furnace heat recovery units. Biochemists are experimenting with its potential use in 3-dimensional form as an ideal material for cell and bone growth.

Lockheed's HTP, (High Thermal Protection), is the improved and implemented third generation of the original material. It's flexibility and potential use invite continued modification for new applications.

RHODIUM-FREE AUTOMOTIVE THREE WAY CONVERTOR

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Since their introduction in the early 80's, all automotive three way catalytic convertors have employed rhodium in order to bring about the efficient catalytic removal of nitrogen oxides from the engine exhaust. Rhodium is a very scarce, strategic precious metal and has been subject to extreme price volatility due to intermittent supply interruptions (see Figure 1); over 85% of the world wide supply of rhodium is used in the manufacture of automotive catalytic convertors. Rhodium containing three way convertors also have a serious drawback in that they cannot withstand the high temperature oxidizing environments which result from the need to mount the catalytic convertor more closely to the engine in order to meet more stringent emission regulations. As a result of the undesirable qualities associated with rhodium containing three way catalysts, Ford Motor Company in joint partnership with automotive catalyst suppliers Engelhard and Johns Matthey embarked on an effort to develop a completely rhodium free three way catalytic convertor.

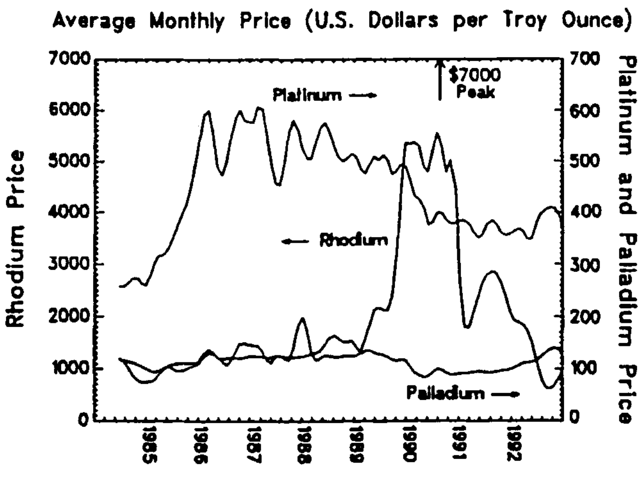

FIGURE 1 Historical prices of the precious metals.

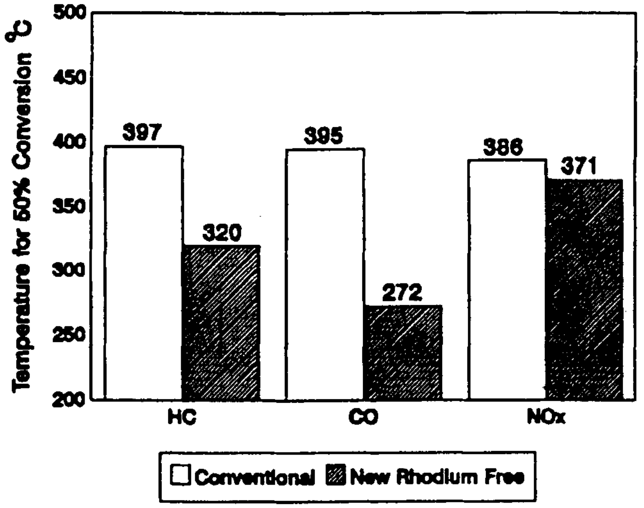

FIGURE 2 Light-off performance of new rhodium free catalyst.

In-house research which was carried out at Ford Motor Company concentrated on the judicious use of alkaline metals and rare earth oxides in conjunction with palladium in order to obtain "rhodium-like" behavior. Palladium was considered to be the metal of choice for replacing rhodium because it is chemically closer to rhodium than platinum and it is relatively more abundant and much more thermally stable compared to platinum. The primary goal of this basic research was to develop or construct a stable catalytic site comprised of specific ions in controlled proximity to both highly dispersed and bulk-like palladium particles. A secondary objective for the work with the alkaline metals and rare earth oxides focused upon increasing the thermal stability of the catalyst washcoat material. After establishing feasibility for a rhodium free three way catalyst, the enabling technology was passed along to Ford's catalyst suppliers, Engelhard and Johnson Matthey, who were invited to participate in a joint development effort.

By the end of the joint development program, Ford's new rhodium free or palladium only three way catalyst technology significantly out performed the current production rhodium containing automotive catalyst technology. The palladium only three way catalyst technology provides for: 1. greatly improved

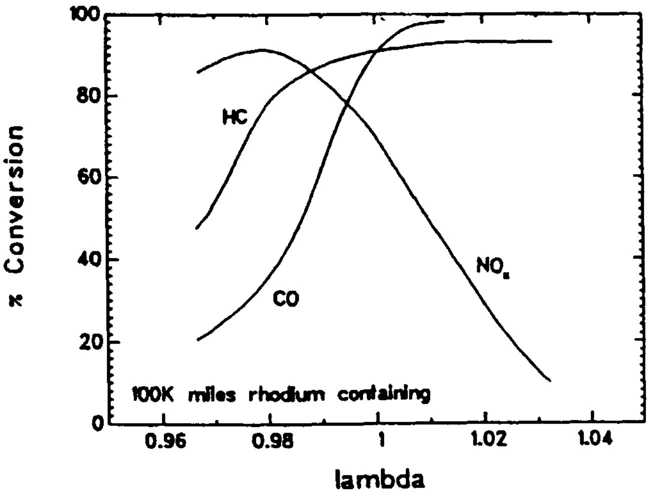

FIGURE 3a Three way performance of conventional rhodium containing catalyst.

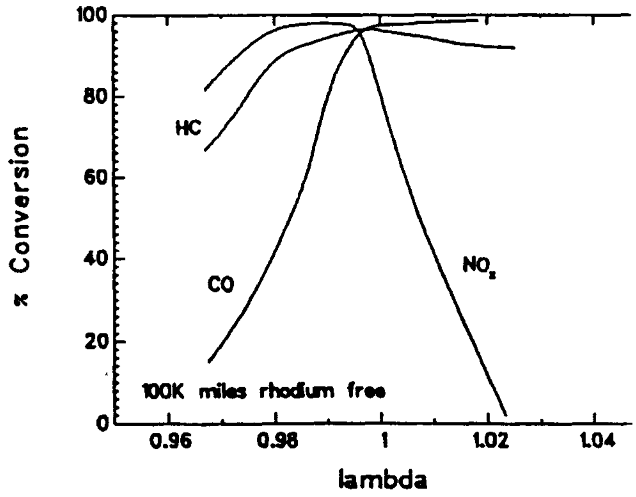

FIGURE 3b Three way performance of new rhodium free catalyst.

light-off performance (see Figure 2) which reduces hydrocarbon cold start emissions and 2. better warmed up three way conversion efficiency (see Figure 3a and 3b). Additionally, the new palladium only technology is significantly more thermally stable than today's rhodium containing catalysts which allows the convertor to be mounted closer to the engine hence enabling more stringent emission regulations to be met.

The new rhodium free automotive catalyst technology which has been developed by Ford Motor Company and its catalyst suppliers provides for significantly reduced automotive tailpipe emissions (see Figure 4). As a result, this technology will play a key role in Ford's strategy for obtaining global leadership in the manufacture of environmentally friendly yet affordable cars and trucks. Ford has released this new catalyst technology on 1995 model year medium heavy duty truck applications. More details associated with this important breakthrough in automotive catalyst technology can be found in SAE Paper #941058.

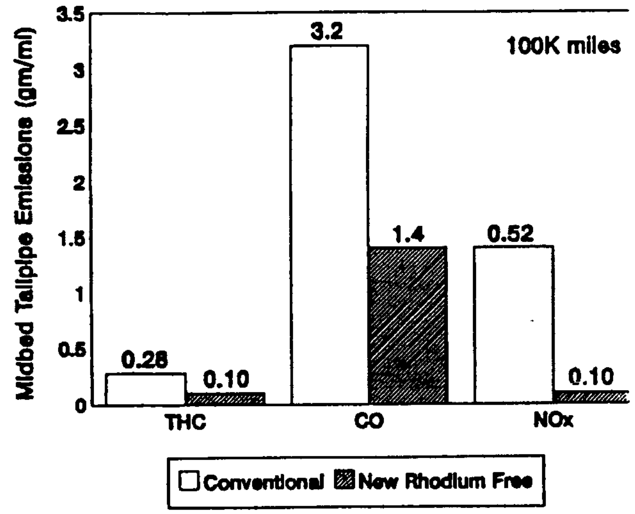

FIGURE 4 Vehicle emissions with new rhodium free catalyst.

THE LITHIUM BATTERY

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The remarkable technical advances enjoyed by modern society are based on our ability to convert energy from one form to another. Moreover, the chemical bond provides a convenient and versatile energy store, which is why the renewable and fossil fuels continue to play such a major role in our economy. A rechargeable (secondary) battery combines chemical-energy storage with the ability to convert the stored energy reversibly and cleanly into electric power.

The oil crisis of the early 1970's prompted a call to the research community to develop alternate energy sources and higher energy efficiencies. Alternate energy sources such as solar power and wind are intermittent and are most effectively used where they can be converted into long-term stored energy; modular energy storage would also be useful for leveling demands on the electric power grid. Moreover, a light-weight rechargeable battery promises to have a growing market in portable computers, communication systems, power tools, and electric vehicles.

An electrochemical cell passes electronic current through an external circuit that must be matched by an internal ionic current as shown in Figure 1. The four essential components of the cell are (1) a negative electrode (the anode), (2) an electrolyte, which must pass the working ion and be an electronic insulator, (3) a positive electrode (the cathode), and (4) a separator permeable to the working ion of the electrolyte that keeps the two electrodes apart within the cell. A solid electrolyte can double as a separator. In a battery, the anode also stores the chemical energy and the cathode stores the product of the chemical reaction between the electrodes. In a rechargeable battery, the chemical reaction must be reversible. The electric power it can deliver is the product of the voltage of the cell times the current it passes at that voltage. Up-grading the voltage and current density of a cell is critical for achieving the weight gains needed for portable power sources.

The familiar lead-acid battery used in cars contains the heavy element lead in both the anode and the cathode. It also depends on slow kinetics to preserve its stored energy while at open circuit. Although it is capable of delivering relatively high power, its ratio of stored energy to total weight is too low for many uses. A lithium rechargeable battery offers higher energy densities as lithium is one of the lighter

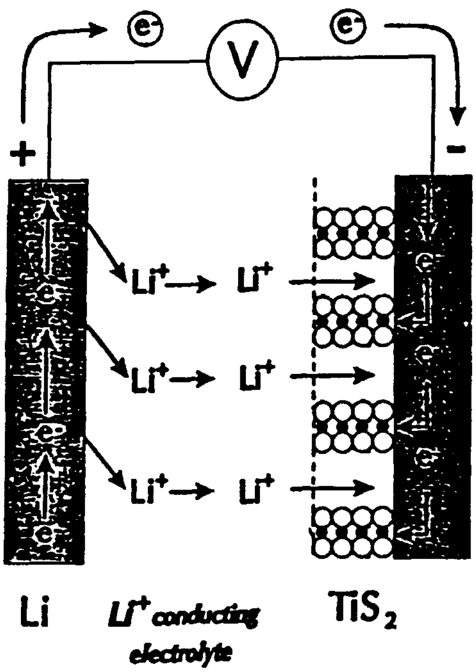

FIGURE 1 Li/TiS$_2$ cell.

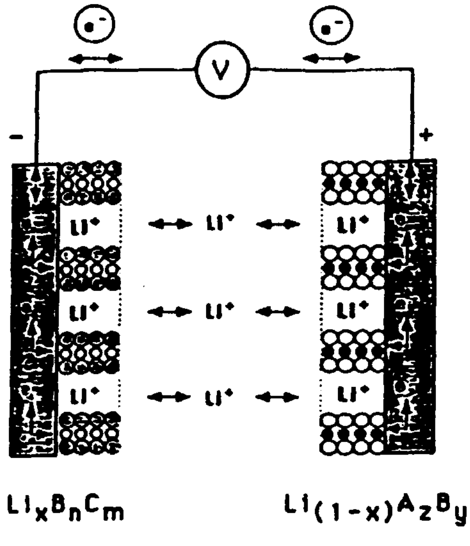

FIGURE 2 "Rocking-chair" cell.

elements; it also offers the possibility of higher voltages stable at open circuit. The primary challenge to the designer of a rechargeable lithium battery was the choice of suitable electrodes chemically matched to a Li^+-ion electrolyte for chemical stability, a large open-circuit cell voltage, and a rapid chemical reaction for delivering a high current density.

The original concept began with a lithium-metal anode and an insertion-compound cathode. An insertion compound is a host into which lithium can be inserted and from which it can be extracted without a change of the basic structure of the host. The feasibility of an insertion-compound cathode was first demonstrated by M. S. Whittingham of EXXON in 1974 with the layered compound titanium disulfide, TiS_2, illustrated in Figure 1; the reaction

$$xLi + TiS_2 = Li_xTiS_2 \tag{1}$$

is reversible for $0 < x < 1$ and it is moderately rapid at room temperature; moreover, it gives a voltage relative to elemental lithium of about 2 V, which is comparable to the lead-acid battery. However, it was soon shown that a lithium-metal anode is not reversible over many cycles. In addition, to make the anode reversible requires lowering the anode potential and hence also the output voltage of a battery using a TiS_2 cathode.

Goodenough recognized that the voltage that can be realized with a sulfide is limited; a higher voltage could be achieved with an oxide. However, a layered oxide MO_2 suitable for lithium insertion is not found in nature. On the other hand, layered $LiMO_2$ compounds were known; the question to be answered was how much Li can be extracted reversibly from an $LiMO_2$ compound. In 1978, Goodenough and coworkers demonstrated that well over half of the lithium can be extracted and reinserted from $LiCoO_2$ over many cycles; moreover voltages in excess of 4 V relative to an elemental lithium anode were found. The concept of a layered $Li_{1-y}MO_2$ cathode having a structure analogous to that of TiS_2 was patented for pairing with a similar insertion-compound anode. Use of insertion compounds for both anode and cathode is referred to as a "rocking-chair" or "shuttle-cock" cell, see Figure 2. Goodenough's group also showed that the Li-insertion reaction in $Li_{1-y}CoO_2$ is nearly an order of magnitude faster than in Li_xTiS_2. In addition, the group developed $Li_{1\pm x}[Mn_2]O_4$ spinels as cathode materials; these are used in primary cells and are under development at Belcore for secondary cells.

Marketing of a secondary lithium battery awaited development of a suitable insertion-compound host for the anode. The Japanese have developed a special graphitic carbon for this purpose, and SANYO Electric Co., Ltd. of Japan, for example, now markets a rechargeable lithium battery using the carbon anode and the oxide cathode that promises to preview a remarkable up-grading of portable rechargeable power sources having a large market potential.

MATERIALS CHALLENGES IN THE DEVELOPMENT OF POLYMER ELECTROLYTE FUEL CELLS FOR TRANSPORTATION*

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A fuel cell is an energy conversion device capable of converting the chemical energy of a fuel directly into electric energy at high efficiency. A simplistic picture of the fuel cell which highlights it's basic function would be that of a "black box" with inlets of fuel (typically, hydrogen) and oxidant (typically, air), and an electric outlet of direct current. The Polymer Electrolyte Fuel Cell (PEFC) is a member of this family of energy conversion devices which has received high attention recently as a potential power source for the next generation vehicle. The reason for this interest is the unique combination of high energy conversion efficiency and very low emission levels which can be achieved with this power source. This is exactly the combination of properties required for the power source of the future vehicle, because it could lower the dependence of the U.S. on oil imports and ensure a cleaner environment. The realistic conversion efficiency, from chemical energy of hydrogen fuel to electric energy, demonstrated for this type of fuel cell when operating at nominal power levels on hydrogen and air, is around

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*This work at LANL has been supported by the U.S. Department of Energy, Electric and Hybrid Vehicle Program, Office of Transportation Technology.

50%. This is, at least, twice the conversion efficiency of an internal combustion engine. Thanks to the very low temperature of operation (around 80°C) and the use of hydrogen fuel, this power source will not emit any hazardous gases like NOx and CO, and is therefore a potential basis for a real Zero Emission Vehicles (ZEV). Furthermore, thanks to the higher efficiency achieved vs. the IC engine, the amount of CO_2 (green house gas) generated per mile driven should also be decreased significantly by introduction of fuel cell powered vehicles, even when considering natural gas as the source for hydrogen fuel.

With this as background, the natural question is: "Why are vehicles today still not powered by PEFCs?" The answer is that, in spite of all the advantages mentioned above, this technology was considered only several years ago unrealistic for wide spread applications in terrestrial transportation. The reasons were the very high cost of the materials and the unproved efficiency and reliability of the device under realistic operation conditions in transportation. *All of these problems have been strongly tied to materials aspects of this technology*. The central challenges in this technology have been reduction of the cost of materials, evaluation of materials properties leading to their modification for specific application in the fuel cell, and identification of new materials or combination of materials for the various components of this type of power source. This presentation describes some important recent steps made at Los Alamos National Laboratory (LANL), that have contributed significantly to the near-future implementation of polymer electrolyte fuel cells in transportation. This has been achieved by answering some key materials challenges.

Materially speaking, the PEFC is a technology of carbon, polymers and precious metal catalysts. The heart of the cell is a polymeric membrane with high ionic (protonic) conductivity which has thin films of catalyst bonded on both it's major surfaces. These films provide the active sites for the electrocatalytic reactions of hydrogen and air, i.e., the sites where chemicals are directly converted to electricity. The first important challenge in the development of PEFC technology for terrestrial transportation has been the reduction of the very high loadings of platinum catalyst which were employed in an earlier version of this technology developed for space applications. The R&D work performed at LANL on the catalyst layer was essentially an effort of optimization of composition and structure of a unique thin film. This optimization effort has been aimed at achieving the highest reactivity of the catalytic processes in the fuel cell electrodes by enabling simultaneous effective access of electronic, ionic and gaseous reactants within this film containing the active sites. Under such optimized conditions, the catalyst loading could be reduced while maintaining high performance. At the same time, such an optimized composite thin film must also exhibit high structural and compositional stability for thousands of hours of cell operation, as well as withstand shocks of freeze-thaw cycles.

Successful optimization of such composite thin catalyst layers has been achieved recently at LANL by intermixing the solubilized membrane material in a special, thermoplastic form with carbon-supported platinum catalyst, drying and effectively bonding the dry composite to the ionomeric membrane either directly or by a decal process. The total effort required only about 5–7 man-years, but the consequences in terms of implementation of this fuel cell technology in transportation were very substantial. The cost of platinum for a complete power source for a passenger car was reduced from $30,000 to just $300. Platinum cost and availability have thus been reduced to secondary issues, opening the way to large-scale applications of PEFC technology.

While the catalyst loading has been so strongly reduced, the performance of the fuel cell on hydrogen on air has been, at the same time, significantly improved. This improvement in performance has required optimization of other components, including the component called "gas-diffuser" or "backing layer" which enables direct access of reactant gases to the thin film catalyst with no excessive transport barriers set by liquid water. This gas-diffuser layer required graded porosity and hydrophobic/hydrophilic intermixed characteristics, all to be achieved in a thin, electronically conducting and corrosion resistant material. Optimization at LANL of gas-diffusers, based on surface treated porous carbon structures, has contributed to the development of efficient air electrodes for PEFCs. A well designed porous gas-diffuser can reduce the gas pressures required to achieve high performance and thus lead to a simplified and less expensive power source. This is an example where materials R&D leads to significant savings in systems complexity and cost.

The work on optimization of the gas diffuser has been performed in collaboration with two U.S. small businesses. This has been a typical mode of operation as the LANL work on advanced and improved materials for PEFC technology has attracted significant interest in U.S. industry, including automotive, chemical and power source industries. As a further example, in our R&D work on the ionomeric membrane—the "heart" of the cell—we have collaborated extensively with manufacturers of this advanced material. Our very detailed characterization of transport and surface properties in these membranes under conditions directly relevant to fuel cell operation, has demonstrated clearly that the two most important modifications required in fuel cell membrane properties are: (i) thinner membranes and (ii) improved water uptake by the membrane from the vapor phase. As a direct consequence of our membrane R&D work, some new commercial products have recently become available that specifically address these needs.

In summary, recent achievements in materials research at LANL have significantly advanced the technology of the polymer electrolyte fuel cell as a viable option for large-scale transportation applications. These achievements amount to a significant contribution to the goal of a future efficient and emission-free vehicle.

NANOCOMPOSITES VIA THE SOL-GEL ROUTE

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WHAT IS A NANOCOMPOSITE? STRUCTURAL AND COMPOSITIONAL DI-PHASICITY

The definition is self-evident: a material consisting of two or more phases in which all (or one) are of nanometer dimensions.

The concept of "nanocomposites" was first conceived[1] and developed by Roy and Komarneni during the period 1980–81, as an alternative goal for solution-sol-gel (SSG) processing of ceramic materials. Up to that point, and in the vast majority of SSG research today, the goal is to make maximally homogeneous ceramics: the radical innovation was to use simple SSG processing to make maximally heterogeneous ceramics. The term "nanocomposites" was also coined by us around 1982–83 to describe such solids as documented in a 1984 publication.[2] Niihara[3] has presented a useful figure (Figure 1) showing the different kinds of nanocomposites one can get in ordinary ceramics.

Nanocomposite materials may consist of *compositionally* or *structurally* di- or multi-phase xerogels, or both *compositionally* and *structurally* di- or multi-phasic materials. The compositionally di- or multiphasic materials are mixtures composed of two or more nanoscale solid phases (which differ in *com-*

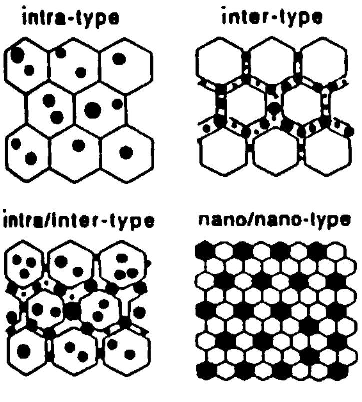


FIGURE 1

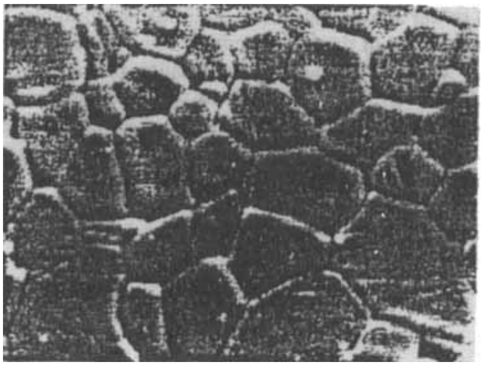


FIGURE 2

position), for example, a mixture of TiO_2 and ZrO_2 sols. A structurally diphasic solid consists of, e.g., nanoscale noncrystalline SiO_2 and nanocrystalline quartz, intimately mixed via SSG.

MAKING NANOCOMPOSITES VIA SSG

The commercial significance of SSG-derived nanocomposites results from the ease of making them. There are two routes to their preparation. In the first two stable sols of selected solid nanophases in the same liquid phase are mixed and co-gelled. Indeed any mixture of solids reduced to nanometer scale by continuous grinding in a fluid medium will have the precursor mixed sol from which on gelling a solid nanocomposite will result. A second method involves the creation of a gel, and the precipitation within the gel of nanometer size crystals by counter diffusion of appropriate anions and cations, or infiltration of organics.[4] Thus this route can give us 0:0 or 0:3 composites of organics and inorganics.

WHY NANOCOMPOSITES WORK

Structural nanocomposites work by catalyzing ceramic reactions via solid state epitaxy resulting in (a) much lower reaction temperature; (b) radically refined microstructure of product; (c) creating different structure ceramics merely by controlling seeding phase. Compositional nanocomposites work by capitalizing on the excess energy stored in the metastable assemblage, lowering reaction temperatures and enhancing the potential of metastable melting.

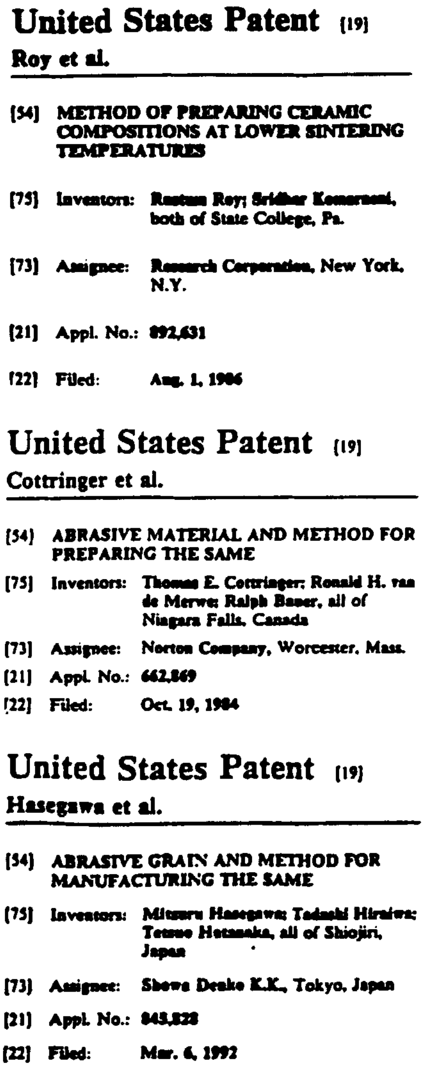
APPLICATIONS

Mullite Powders

Using mullite, $Al_6Si_2O_{13}$, and cordierite, $Mg_2Al_4Si_5O_{18}$, as prototype models, we showed[5-8] that the *compositionally* diphasic and triphasic materials sinter to crystalline products with theoretical density at a much lower temperature than the single phase gels of the conventional SSG process. This innovation in ultrafine powder design has led to the commercial production of advanced mullite powder by Chichibu Cement Co. Ltd., Japan. About 1–2 tons of this powder are sold per month and used for producing rollers, chain belts, refractories, etc., for high temperature kilns. Figure 2 shows Chichibu's fully densified mullite using this nanocomposite approach.

Abrasive Grains

Structural seeding of gels via epitaxial effects had been proven and practiced in our lab for 30 years in hydrothermal reactors. Our new work showed that such structural nucleation in the same Al_2O_3 sols could be achieved in ordinary dry ceramic reactions, to lower crystallization temperatures in the Al_2O_3 and $MgO\text{-}Al_2O_3$ system.[9] Kumagai and Messing[10] showed how the densification was enhanced. The technological application to abrasive grain has spread rapidly across the industry with several patents



United States Patent [19]
Roy et al.

[54] METHOD OF PREPARING CERAMIC COMPOSITIONS AT LOWER SINTERING TEMPERATURES

[75] Inventors: Rustum Roy; Sridhar Komarneni, both of State College, Pa.

[73] Assignee: Research Corporation, New York, N.Y.

[21] Appl. No.: 892,631

[22] Filed: Aug. 1, 1986

United States Patent [19]
Cottringer et al.

[54] ABRASIVE MATERIAL AND METHOD FOR PREPARING THE SAME

[75] Inventors: Thomas E. Cottringer; Ronald H. van de Merwe; Ralph Bauer, all of Niagara Falls, Canada

[73] Assignee: Norton Company, Worcester, Mass.

[21] Appl. No.: 662,869

[22] Filed: Oct. 19, 1984

United States Patent [19]
Hasegawa et al.

[54] ABRASIVE GRAIN AND METHOD FOR MANUFACTURING THE SAME

[75] Inventors: Mitsuru Hasegawa; Tadashi Hiraiwa; Tetsuo Hatanaka, all of Shiojiri, Japan

[73] Assignee: Showa Denko K.K., Tokyo, Japan

[21] Appl. No.: 843,828

[22] Filed: Mar. 6, 1992

FIGURE 3

(including ours)[9,11,12] filed by U.S. (Norton and 3M) and Japanese (ShowaDenko) companies, all based on seeded gels (Figure 3).

OTHER CERAMICS

Niihara[3] has shown the major advantages of nanocomposites in high strength ceramics of Al_2O_3, Si_3N_4, SiC, etc.

Organic-Inorganic

Organic-inorganic nanocomposites were first used in our lab for SiO_2-photoresist patterning.[4] Endo et al.[13] have used such to enhance the luminescence output from clay-rhodamine nanocomposites. Pope and Mackenzie have made various 0:3 SiO_2-organic nanocomposites with interesting optical properties.

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THE DEVELOPMENT OF COMPGLAS® FIBER REINFORCED GLASS-CERAMICS

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Gary Linsey and Craig Musson, Pratt & Whitney

INTRODUCTION

The development of fiber reinforced glass-ceramic matrix composites has been spurred by the desire to create low density, durable materials whose exceptional performance, ease of fabrication and low cost enable significant advances in both aerospace and industrial applications.

Two emerging trends in materials technology were key to the success of this endeavor. First, that carbon fiber reinforced polymer matrix composites were becoming widely accepted, and that their complex failure modes provided sufficient reliability in service despite their lack of "ductility." Second, the emergence of high strength ceramic fibers, particularly in the U.S. and Japan, whose oxidative stability permitted their use at high temperatures beyond the capability of carbon fibers.

Our approach was to develop a technology that could benefit from the past experience and existing infrastructure for polymer composites and that would be able to find broad enough applicability to be both technically and financially successful.

TECHNOLOGY DEVELOPMENT

The development of this materials technology, specifically for gas turbine engines, has required progress simultaneously on three key fronts.

Compositional Development

The use of glass-ceramics as matrix materials has been key. While readily available and low cost, their compositions had to be developed specifically to meet processability and performance requirements.

Ceramic fibers also are available. However, their compatibility with specific matrices and the need for high temperature oxidation resistance necessitated the development of environmentally stable fiber coatings and fiber/matrix interfaces. Through the creation of these interfaces, it is possible to achieve

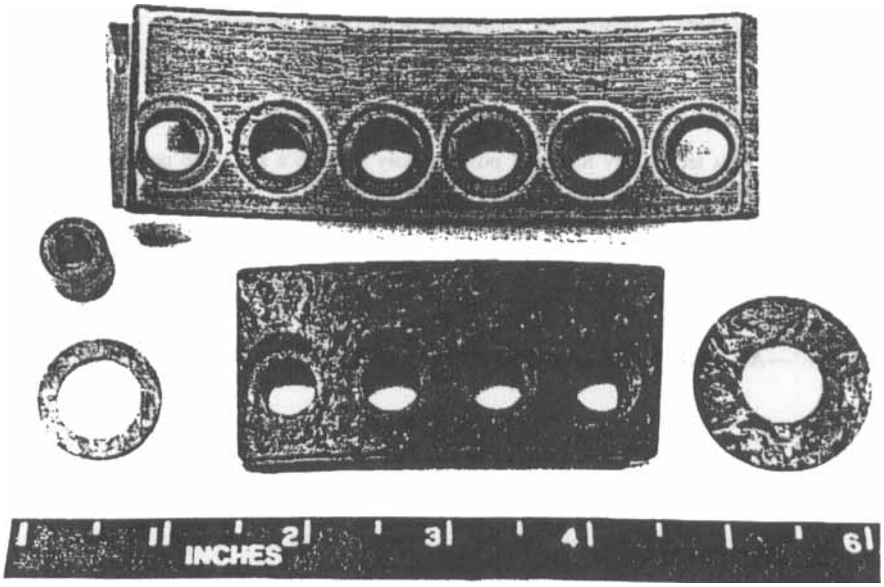

FIGURE 1 Gas turbine UT-15 COMPGLAS® components currently operating at temperatures of up to 800°F.

fracture behavior similar to that of carbon fiber reinforced epoxy systems, but at much higher temperatures.

Component Fabrication Techniques

It was recognized early on that processes needed to be developed which can produce the complex shapes required in real applications at affordable cost. Our approach was to develop a range of processes that involved a wide range of fiber architectures and preforms. This process capability was essential to the demonstration of engine component performance.

Component Demonstration

Only through the evaluation of real components in both rig and engine testing were we able to deduce the combined effects of applied stress and operating environment on composite behavior. The results of these tests were key in developing optimum compositions for successful gas turbine application.

APPLICATIONS

We have developed a wide range of composite compositions that we refer to as COMPGLAS®. For gas turbine applications, we have two particular systems that are finding key applications.

Low Temperature/Low Stress Applications

A composite, UT-15, tailored specifically to perform in applications requiring excellent wear resistance at temperatures of up to approximately 1500°F (800°C) was developed and is currently in engine application. Through the use of low volume percents of chopped, discontinuous fibers, we are able to fabricate complex shapes that operate at temperatures well above those of polymer matrix composites, Figure 1; however, at a cost less than that of high temperature PMC's.

High Temperature/High Stress Applications

A composite, UT-22, whose glass-ceramic matrix and fiber-matrix interface has been tailored specifically for highly stressed, high temperature applications possesses useful structural characteristics up to approximately 2200°F (1200°C). Selected for combustor applications, this system has demonstrated durability under stress for times exceeding 10,000 hours.

ACKNOWLEDGMENT

The emergence of this technology has been possible only through a sustained partnership involving United Technologies Corporation funding and the support of U.S. Government agencies, particularly the Office of Naval Research and the Air Force Wright Laboratories.

'STARLITE'—A UNIQUE, HEAT-RESISTING, INSULATING, POLYMERIC MATERIAL

MAURICE WARD
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HEAT-RESISTING PLASTICS

In 1985 Maurice Ward, prompted by the Manchester air disaster in which 54 people perished mainly due to the inhalation of toxic smoke from burning polymeric materials, commenced work on the formulation of new fire-retardent plastics. With 10 years of plastic compounding and fabrication experience, working in his small factory producing polythene sheet products and with little formal academic training, Maurice Ward began to blend various organic and inorganic compounds to try and develop heat-resisting plastics, the Holy Grail of polymer scientists.

Of the 3 basic materials: metals, ceramics and polymers, metals and ceramics are well developed as heat-resisting materials for applications in the temperature range 1000° to 2000°C whereas most plastics are unable to resist heat at temperatures much above 100°C. Plastics however have better formability and are much lighter in weight than metals and ceramics. Another important property of materials is heat conductivity or conversely, insulation capability. Metals, by definition, are good conductors whereas ceramics and plastics are almost always insulating materials.

EARLY EXPERIMENTS

By April 1986 Maurice Ward had produced the first heat-resisting plastic, which he called Starlite, in bulk form as a thermoplastic sheet. By 1989 further development resulted in Starlite formulations which could be used as surface coatings for a wide range of components and substrate materials.

Starlite materials are multi-component organic and inorganic systems set in a conventional polymeric matrix to produce polymer composites capable of withstanding flame temperatures of at least 1000°C. Initial testing examined the combustion behaviour of simple materials such as cloth, paper, carpet, nylon, kevlar, polypropylene and stainless steel mesh in the uncoated and Starlite-coated conditions. In every case Starlite coating prevented burning and the emission of smoke and toxic fumes. Remarkable also was the observation that Starlite acted not only as a flame barrier but also as an insulating heat barrier preventing the underlying substrates from getting hot.

THE FIRST TRIALS

With the original requirement of developing flame resisting plastics for aircraft interiors, tests were carried out on British military and civil aircraft components in early 1989 with outstanding success.[1] Starlite-coated materials withstood flame temperatures of 1200°C and hot air blower temperatures of 600°C with negligible smoke and toxic gas release. Further heat release tests for aircraft interiors confirmed that Starlite imparts fire barrier, flux heat and radiant heat barrier properties.[2] Starlite was thus authenticated as a flame-resisting material and as a high temperature insulating material.

LASER AND NUCLEAR RESISTANCE

Subsequent research on the applications and properties of Starlite have indicated that Starlite has adaptive protective properties towards laser radiation and high energy radiation produced in simulated nuclear flash conditions.[3] Starlite somehow resists penetration by these energy forms which for example would penetrate or evaporate conventional materials such as stainless steel. These tests were carried out in Government military and nuclear establishments in the period 1990 to 1993.

EVERYDAY APPLICATIONS

As described above, the new material has been seized upon by defence and aerospace organisations where strategic materials are in great demand but much more general applications are envisaged for Starlite. There are enormous implications for everyday life in producing heat-resisting insulating plastics as bulk materials or as coatings on other materials. Immediate potential applications include fire protection and insulation of buildings, structures, security items, electrical cables, electronic circuit boards in safety critical applications and fabrics for furnishings and clothing.

SECRECY, EXPLOITATION AND BASIC SCIENCE

As might be expected, Starlite formulations and precise commercial applications are subject to a high degree of secrecy due to the wealth-creation prospects for such an outstanding discovery but at the same time there has been general acclaim with the international press, popular science articles and TV programmes world-wide reporting the invention of Starlite with enthusiasm. For example in the BBC TV Tomorrow's World programme[4] a hen's egg coated with Starlite did not cook when heated with a flame torch producing 1200°C.

Although systematic testing has been carried out in Government and commercial research centres to assess the performance of Starlite, there is still a large amount of research and development necessary to optimise the properties and to investigate the self-immunising, surface protection mechanism. Preliminary research[5] has indicated that subsurface layers of minute gas-filled bubbles and the formation of a plasma of ionised gas at the surface of the Starlite provide a protection barrier to incident radiation.

Starlite has been invented, developed and tested in the short space of less than 10 years. The next decade should see significant commercial exploitation and scientific research into this unique material.

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