



Solid Electrolyte Materials, Devices, and Applications

ASHOK V. JOSHI, JAMES J. STEPPAN,* DALE M. TAYLOR & S. ELANGO VAN

Ceramatec, Inc., 2425 South 900 West, Salt Lake City, UT 84119

Submitted April 18, 2003; Revised March 26, 2004; Accepted March 30, 2004

Abstract. This paper outlines the development status, issues, and applications of several solid electrolyte electrochemical devices currently being developed by Ceramatec and its partners. Ceramatec and its commercial partner Air Products and Chemicals, Inc., (APCI) have successfully developed and demonstrated an electrochemical device that utilizes a ceria-based, solid electrolyte to separate oxygen from air [1, 2]. Other oxygen separator projects utilize ion transport membrane(s) (ITM) composed of mixed ionic and electronic conductors to transport oxygen ions across the membrane by means of a pressure differential driving force to generate high purity oxygen or a chemical reaction driving force to produce synthesis gas from methane (ITM Syngas).

Ceramatec, in partnership with SOFCo, demonstrated kilowatt class solid oxide fuel cell (SOFC) stacks operating on a variety of fuels such as pipeline natural gas and reformed diesel. Ceramatec is presently working with Cummins and SOFCo to develop low cost modular fuel cells under the Department of Energy's Solid-state Energy Conversion Alliance (SECA) initiative. Some of Ceramatec's other programs are focused on development of gallate electrolyte based fuel cells [3] and metallic bipolar plates [4] for lower temperature operation.

Keywords: fuel cells, ion transport membranes, oxygen separators, solid state ionic devices

1. Introduction

Ceramatec and its commercial partners have been developing ITMs for a wide range of applications. This paper outlines the status of oxygen ITMs and devices being developed, demonstrated, and commercialized for the following applications: (1) Electrolytic oxygen separation using ionically-conducting ITMs; (2) Galvanic oxygen separation using ionically-conducting ITMs for SOFCs; (3) Pressure-driven oxygen separation using mixed-conducting (electronic + ionic) ITMs; (4) Chemical synthesis combined with oxygen separation using mixed-conducting ITMs.

2. Electrolytic Oxygen Separation using Ionically-Conducting ITMs

Ceramatec and APCI have significant experience developing ceramic solid electrolyte oxygen separa-

tion (SEOS) devices [5–14]. The SEOS technology is based on the principle of oxygen ion migration through a dense ceramic electrolyte membrane under the influence of an externally applied electrical potential. Removal of the oxygen product from the anode side of the electrolyte membrane results in the continuous production of pure oxygen. The SEOS process utilizes an electrochemical stack [11] fabricated from high-temperature conductive ceramic materials to produce high purity oxygen at elevated pressure from a feed stream of ambient pressure air.

2.1. Ionically-Conducting ITM (Electrolyte)

The SEOS solid electrolyte is based on cerium oxide, with dopants added to enhance both ion transport and membrane processability. The device must be operated at temperatures above approximately 600°C to achieve sufficient oxygen ion conductivity through the electrolyte. At these temperatures, doped ceria exhibits a significant performance advantage over zirconia-based

*To whom all correspondence should be addressed. E-mail: jsteppan@Ceramatec.com

materials. For example, the conductivity of Gd-doped ceria at 800°C is about 0.1 S/cm, and is approximately one order of magnitude higher than that of YSZ [15, 16]. The use of a ceria-based electrolyte can be problematic in some electrochemical applications due to the tendency of CeO₂ to undergo reduction from Ce⁴⁺ to Ce³⁺ under reducing conditions [17], but this is not the case for SEOS applications as oxidizing environments are present on both the anode and cathode sides of the electrolyte.

The ionic conductivity of pure ceria is negligible. Incorporation of divalent and trivalent dopants into the fluorite CeO₂ structure increases the concentration of oxygen ion vacancies, as required by overall charge neutrality. A wide variety of dopants have been evaluated for improving the ionic conductivity of ceria [18]. The strongest enhancement to the ionic conductivity of ceria appears to result from doping with rare earth oxides, of which gadolinia and samaria have been reported to yield the best results. For example, the reported ionic conductivity of these materials at 800°C is approximately 0.08 S/cm [15]. The presence of silica and other contaminants influence the dopant level required for optimum ionic conductivity [19].

A commercially viable electrolyte must be dense (greater than 95% of theoretical density) and have no connected through porosity. In addition, an electrolyte composition that requires a sintering temperature above 1600°C to attain a high density adds additional cost and complexity to the manufacturing process making it commercially impractical. Therefore, “sintering aids” may be employed to lower sintering temperatures while still attaining the required high density without compromising performance. For rare earth-doped ceria, titanium oxide is an effective sintering aid. Additional details about ceramic processing methods employed for the manufacture of the electrolyte can be found elsewhere [1].

2.2. *Electrodes*

The oxidation and reduction reactions are promoted by the use of bifunctional, porous perovskite electrodes, which together with the electrolyte, form an electrochemical cell. The electrodes are specifically chosen for their ionic and electronic conductivity and catalytic activity. One class of electrode material that can satisfy the principal requirements is lan-

thanum strontium cobaltite. This powder was made into an ink with appropriate solvents and applied to the electrolyte by conventional screen printing or similar methods.

Electrochemical impedance spectroscopy (EIS) was employed to evaluate the ohmic and non-ohmic contributions to the resistance of an operating electrochemical cell (electrolyte plus electrodes). EIS test data have established cell performance over thousands of hours and have enabled optimization of electrolyte and electrode characteristics. Operational data for cells was obtained based on Sr-doped and rare earth-doped ceria electrolyte at 750°C. In these experiments, cells were fabricated with varying electrolyte thickness, and the ohmic component of the area specific resistance (ASR) was determined as a function of electrolyte thickness. The ionic conductivity of the rare earth-doped ceria was 0.059 S/cm and was superior to that of the Sr-doped ceria at 0.044 S/cm.

2.3. *Interconnects and Stacks*

Each electrochemical cell is in contact with a dense interconnect made from an electronically conductive perovskite material. The cell-interconnect subassembly is termed a couple and is the repeat unit for constructing a SEOS stack. The interconnects conduct electronic current through the stack and provide the mechanical support for a planar ITM SEOS device. Interconnects, like all stack materials, must be carefully selected to meet criteria for thermal expansion match, chemical compatibility, and mechanical robustness, as well as for ionic and electronic conductivity. Each interconnect is featured to provide appropriate passages for the feed and product streams. In contrast to the electrolyte, the interconnect must be an ionic insulator and an electronic conductor. Additional details regarding the development of the perovskite interconnect materials can be found elsewhere [20, 21].

2.4. *Couple and Stack Seals*

The repeat units (couples) of the ITM SEOS stack, connected electrically in series, must be sealed on the anode (oxygen) side to form connected, gas-tight passages for the oxygen product. The development of robust seal materials, designs, and processes are critical

to the long-term performance and reliability of a SEOS stack and have been discussed in detail elsewhere [1, 12, 13].

2.5. Stack Performance

SEOS stacks comprising multiple cells in a planar configuration have demonstrated excellent electrochemical performance and stability, mechanical integrity, and the capacity to produce high purity oxygen over thousands of hours. SEOS 3-cell stack have been tested for more than 20,000 hours with relatively low degradation rates of less than 0.5% per 1000 hours.

The theoretical oxygen production in a stack is determined by the Nernst equation [22]. Previous results [1] from 3-cell test stacks show excellent agreement between the actual oxygen production rate and the theoretical prediction. SEOS stacks can be operated using either a voltage or current controller to directly regulate the rate of production of oxygen molecules. This feature allows precise and simple control of gas-flow rates. The response times are instantaneous, compared to the much slower separation mechanisms inherent in molecular sieve and cryogenic distillation technologies.

Analytical techniques employing a high sensitivity discharge ionization detector have indicated a purity of greater than 99.99% for oxygen produced by a SEOS stack. Other tests indicate that feed stream contaminants, including live chemical agents, are not found in the oxygen product stream or in the oxygen-depleted air stream. Similar results would be expected for other carbonaceous contaminants, such as hydrocarbons and biological agents. The chemical analysis results indicate that SEOS technology is capable of producing ultra-high purity (>99.9%), sterile oxygen from air at either atmospheric pressure or reduced pressure (e.g., air at high altitudes). Oxygen generated by SEOS devices will be free of moisture, oils and hydrocarbons, solid particulates, bacteria and biological agents, and all chemical gases and/or agents found in air because only oxygen ions are transported through the ITM and because the membrane operating temperature is high.

One or more electrochemical stacks are integrated with a thermal management system, air mover, power supply, and control systems to form a SEOS oxygen generator. Additional details regarding the design and

implementation of the balance-of-device components have been described elsewhere [1].

3. Galvanic Oxygen Separation using Ionically-Conducting ITMs for SOFCs

SOFCs utilize oxygen ion ITMs as part of a galvanic cell to produce electricity from fuel, while SEOS technology utilizes oxygen ion ITMs as part of an electrolytic cell to produce oxygen using electricity. Yttria-stabilized zirconia (YSZ) has high oxygen ion conductivities at high temperatures (800 to 1000°C). Operation of a fuel cell at such high temperatures increases the complexity and cost of SOFC development, components, and balance of device. Thus, lowering the operating temperature will likely provide a more expeditious route to commercialization of SOFC-based power systems. An intermediate operating temperature range (600 to 800°C) allows the use of lower cost materials in both the stack and the balance of plant, significantly reduces potential deleterious materials interaction, and extends the useful stack life. When the operating temperature is in the range of 600 to 700°C, it is also possible to reform hydrocarbon fuels within the stack. The endothermic nature of this reaction provides a significant cooling effect, thereby reducing the parasitic losses associated with excess air requirements for stack cooling.

3.1. Electrolyte for SOFCs Operating at Intermediate Temperatures

The operating temperature of SOFC is largely governed by the electrolyte material. Electrolyte materials such as doped bismuth oxide or doped ceria exhibit superior ionic conductivity over YSZ at lower temperatures [16]. However, the material instability of bismuth oxide and the mixed conduction of ceria under fuel gas conditions are difficult to overcome. Sr and Mg doped LaGaO₃ (LSGM) has been shown to have an ionic conductivity at 800°C equivalent to that of YSZ at 1000°C. Unlike other materials possessing a high oxygen ion conductivity, lanthanum gallate is stable in both fuel and air. Ishihara et al., reported a power density of ~0.35 W/cm² at 800°C in single cells [23]. Goodenough et al. [24, 25] have reported extensive materials characterization information.

The degradation of the electrochemical performance of LSGM-based cells limits its use by SOFC

developers. The degradation of LSGM single cells occurs primarily at the anode-electrolyte interface. The formation of an insulating phase, LaNiO_3 , at the anode-electrolyte interface is the likely cause of degradation [25]. In addition to long-term stability, the reactivity of the anode and electrolyte limits the cell fabrication options. For example, an anode-supported thin electrolyte approach that has been successfully demonstrated in zirconia-based cells cannot be readily employed. To date, only electrolyte-supported cells have been fabricated for cells with gallate electrolyte. A zirconia matrix supported thin gallate electrolyte has been reported [26]. Again, the reactivity with zirconia to form a lanthanum zirconate insulating phase at the interface is of concern.

Ceramatec's technical approach is to understand the temperature limits of the anode-electrolyte reaction and modify the anode material to mitigate such reactions. In sintering studies using powder mixtures of LSGM and NiO, we found that both the severity of the reaction and the nature of the second phase depends on the reaction temperature. At 1250°C, the reaction phase formed was La_2NiO_4 , while the predominant phase at 1350°C was LaNiO_3 . A chemical modification to the anode reduced the reaction considerably [27]. The modified anode composition is also shown to perform equivalent to standard NiO-based anode. Recent focus has been to lower the sintering temperature of LSGM electrolyte material and evaluating sintering of anode-electrolyte bi-layers.

3.2. *Interconnects for SOFCs Operating at Intermediate Temperatures*

Similar to interconnects for the SEOS oxygen generator, SOFC interconnects must simultaneously satisfy several functional requirements. The challenges in interconnect development must be addressed using a combination of materials, processing, and design in order to achieve low cost and high performance. In contrast to conventional monolithic interconnects, Ceramatec has developed a compliant interconnect design [28]. The design allows separation of the structural and electrical functions, enabling selection of materials best suited to each function and atmosphere. Interconnect materials must have high electronic conductivity for the series electrical connection of individual cells, gas impermeability to separate fuel and oxidant gases, chemical stability and conductivity over a large oxygen con-

centration range. In addition, thermal expansion match with the rest of the cell elements is desired. A metallic interconnect is very suitable for achieving high electrical conductivity and gas impermeability. It also lends itself to ease of fabrication of gas channels and eliminates problems associated with the non-conformity of planar components. The high thermal conductivity of metal interconnects will help distribute the heat generated during the operation of the cell, thereby lowering the cooling air requirement as well as improving temperature uniformity.

The use of metal interconnects poses considerable challenges. Typical austenitic or ferritic materials undergo rapid corrosion at the temperatures of SOFC operation, leading to large and unacceptable increases in resistance. While high Cr alloys match the thermal expansion coefficient of zirconia, the evaporation of Cr species degrades SOFC performance [29]. To mitigate this problem, the metal interconnect was coated with a perovskite such as lanthanum manganite or chromite, which imparts oxide scale conductivity and suppresses the Cr evaporation. We found that ferritic alloys that form a Cr_2O_3 scale offer good oxidation resistance with appropriate surface treatment, permitting their use in SOFC applications.

Surface treatment of the native metal surface along with controlled oxidation was found to provide two benefits: well-adhered oxide scale and a significant reduction in oxide scale growth rate. The oxide scale was also found to provide an intimate interface with the perovskite coating that was applied and heat treated in a subsequent operation. Using the best combination of treatments and coatings appropriate for the anode and cathode atmospheres, the resistance of coupon couples was measured in air and in humidified hydrogen. In humidified hydrogen, the resistance is well below 1 milliohm-cm² while in air it is less than 10 milliohm-cm². Additionally, the coupon couples have been subjected to several thermal cycles and were found to exhibit good stability.

4. **Pressure-Driven Oxygen Separation using Mixed-Conducting ITMs**

The ITM oxygen process uses mixed-conducting ceramic membranes that have both electronic and oxygen ionic conductivity when operated at high temperature, typically 800 to 900°C. Under the influence of an oxygen partial-pressure driving force, the

ITM Oxygen process achieves a high-purity, high-flux separation of oxygen from a compressed-air stream. Thin-film, multi-layer membrane structures capable of supporting the pressure load have been successfully developed. Additional details regarding materials, structures, processes, applications and integration appear elsewhere [30–36]. The process operating conditions are a medium-pressure (100 to 300 psig) air feed stream and a low-vacuum oxygen permeate stream. By integrating the energy-rich, oxygen-depleted, non-permeate stream with a gas turbine system, the ITM Oxygen process becomes a co-producer of high-purity oxygen, power, and steam.

The ITM Oxygen project team includes Air Products and Chemicals, Inc., Eltron Research, Inc., Ceramatec, Inc., ChevronTexaco Inc., Concept NREC Inc., McDermott International, Inc., The Pennsylvania State University, and the University of Pennsylvania. The goal of the three-phase program is to reduce the cost of oxygen production by approximately one-third compared to conventional, competing technologies and demonstrate all necessary technical and economic requirements for commercial scale-up. The 3-phase ITM Oxygen project will develop, scale-up, and demonstrate a novel air separation technology for large-scale production of oxygen from air with the co-production of power, and for the integration of ITM Oxygen with IGCC and other advanced power generation systems.

4.1. ITM Oxygen Membranes

The ITM Oxygen process uses nonporous, mixed-conducting ceramic membranes that have both electronic and oxygen ionic conductivity when operated at high temperature, typically 800 to 900°C. The mixed conductors are complex formulations of inorganic mixed-metal oxides (e.g. perovskites such as $(\text{La},\text{Sr})(\text{Fe},\text{Co},\text{Cu})\text{O}_{3-x}$) that are stoichiometrically deficient of oxygen, causing a distribution of oxygen vacancies in their lattice. Oxygen from the air feed adsorbs onto the surface of the membrane, where it dissociates and ionizes by electron transfer from the membrane. The oxygen anions fill vacancies in the lattice structure and diffuse through the membrane under an oxygen chemical-potential gradient, applied by maintaining a difference in oxygen partial pressure on opposite sides of the membrane. Meanwhile, an internal electronic countercurrent accompanies the

oxygen anion transport. At the permeate (exit) surface of the membrane, the oxygen ions release their electrons, recombine, and desorb from the surface as molecules. Since no mechanism exists for transport of other species, the separation is 100% selective for oxygen, in the absence of leaks, cracks, flaws, or connected through-porosity in the membrane.

The solid-state diffusion of oxygen anions through mixed conductors is well-documented in the literature. The ratio of oxygen partial-pressure on the feed side to the exit (permeate) side of the membrane is the driving force for the oxygen flux. The inverse relationship between oxygen flux and membrane thickness requires that ITM Oxygen components comprise *thin-film* structures capable of supporting the pressure differential necessary to develop the oxygen partial-pressure driving force.

5. Chemical Synthesis Combined with Oxygen Separation using Mixed-Conducting ITMs

The ITM Syngas Team led by Air Products and Chemicals and including Ceramatec, ChevronTexaco, Eltron Research, McDermott Technology and other partners, in collaboration with the U.S. Department of Energy, is developing ceramic Ion Transport Membrane (ITM) technology for the production of synthesis gas and hydrogen from natural gas. The ITM Syngas technology is in the fifth year and Phase 2 of a co-funded \$90 M, nine-year, three-phase development program.

The ITM Syngas process combines air separation and high-temperature syngas generation processes into a single, compact ceramic membrane reactor, resulting in significant savings when compared to conventional technology. Additional details regarding the ITM Syngas process and its advantages over other technologies appear elsewhere [37–41]. In contrast to conventional oxygen-blown Autothermal Reformer (ATR) processes that require high-pressure oxygen typically supplied by a cryogenic Air Separation Unit (ASU), the ITM process uses low pressure air directly, resulting in significant capital and operating cost savings.

5.1. ITM Syngas Membranes

ITM Syngas membranes are fabricated from nonporous, multi-component metallic oxides that operate

at high temperatures and have exceptionally high oxygen flux and selectivity. The membrane structure incorporates a non-porous ITM and reduction and reforming catalyst layers. The membrane material must show long-term stability in reducing and oxidizing atmospheres, and long-term compatibility with the reduction and reforming catalysts.

Stable ITM Syngas material compositions have been successfully developed and planar membranes have been fabricated from these materials. The membranes are based on microchannel device designs developed by Air Products, Ceramtec, and McDermott and are fabricated at Ceramtec using methods that provide good scalability for commercial application. Laboratory-scale membranes have been used extensively to evaluate the properties and performance of candidate ITM materials developed by Air Products, Ceramtec, and Eltron Research. Several generations of ITM Syngas material compositions have been evaluated and compositions that achieve the commercial flux targets have been identified.

Development activities at Ceramtec have also focused on the implementation of fabrication processes to produce large area membranes. These activities have led to a rapid development of scalable fabrication processes and a nearly 200-fold increase in the area of membranes that can be fabricated.

6. Conclusions

Significant progress has been made to develop the four oxygen ion ITM technologies covered in this paper. The SEOS point-of-use oxygen generator technology is closest to commercialization as prototypes have been produced and demonstrated to provide outstanding long-term performance for several years. Efforts to establish a medium-temperature SOFC with gallate-based electrolyte and metal interconnects look promising. These technologies are critical enabling technologies for future SOFCs. ITM Oxygen and ITM Syngas technologies continue to make good progress as membrane modules and seal assemblies have been fabricated and tested and ceramic fabrication scaleup is continuing the progression from lab-scale to full-size membranes. Excellent progress continues to be made against the remaining technical challenges in the demonstration and scale-up of all ITM technologies.

Acknowledgments

The authors gratefully acknowledge support of commercial partners (Air Products and Chemicals Inc., ChevronTexaco Energy Research and Technology Co., Eltron Research Inc., McDermott Technology Inc., and SOFCo, Inc.), funding agencies (US. DOE and DoD), and our colleagues at Ceramtec who support these activities. The development of the four oxygen ion ITM technologies covered in this paper have resulted from the concerted effort of capable teams of researchers, engineers, and technicians. The authors gratefully acknowledge the technical contributions of J. Abrardo, P. Armstrong, D. Brengel, M.F. Carolan, C.M. Chen, P.N. Dyer, R.E. Richards, S.L. Russek, S.W. Rynnders, and others at Air Products, and of S.B. Adler, S. Balagopal, I. Bay, J.R. Chase, R.A. Cutler, M. Flinders, J. Gordon, J. Hartvigsen, B. Heck, B. Henderson, R.A. Hollis, D. Larsen, R. Lashway, J. Pike, F.P. Skeele, M. Timper, M.E. Wilson, M. Zoetmulder, and others at Ceramtec.

References

1. D.L. Meixner, et al., *J. Electrochem. Soc.*, **149**(9), D132 (2002).
2. P.N. Dyer, et al., *Solid State Ionics*, **134**, 21 (2000).
3. S. Elangovan et al., in *Proc. SOFC VIII* (The Electrochemical Society, Pennington, NJ, 2003).
4. S. Elangovan et al., in *Proc. SOFC VIII* (The Electrochemical Society, Pennington, NJ, 2003).
5. A.V. Joshi, U.S. Patent 4,879,016, Nov. 7 (1989).
6. A.V. Joshi, et al., U.S. Patent 5,021,137, June 4 (1991).
7. J.A. Nachlas, et al., U.S. Patent 5,298,138, March 29 (1994).
8. J.A. Nachlas, et al., U.S. Patent 5,338,623, Aug. 16 (1994).
9. D.M. Taylor, et al., U.S. Patent 5,378,345, Jan. 3 (1995).
10. J.A. Nachlas, et al., U.S. Patent 5,479,700, Jan. 2 (1996).
11. M.F. Carolan, et al., U.S. Patent 5,750,279, May 12 (1998).
12. S. Adler, et al., U.S. Patent 5,868,918, Feb. 9 (1999).
13. S. Adler, et al., U.S. Patent 6,042,703, March 28 (2000).
14. S. Adler, et al., U.S. Patent 6,117,288, Sept. 12 (2000).
15. H. Inaba and H. Tagawa, *Solid State Ionics*, **83**, 1 (1996).
16. S.J. Skinner and J.A. Kilner, *Materials Today*, (31-37), March (2003).
17. S.P.S. Badwal, F.T. Ciacchi, and J. Drennan, *Solid State Ionics*, **121**, 253 (1999).
18. M. Mogensen, N.M. Sammes, and G.A. Tompsett, *Solid State Ionics*, **129**, 63 (2000).
19. J.M. Ralph and J.A. Kilner, in *Solid Oxide Fuel Cells V (SOFC V)*, edited by U. Stimming, S.C. Singhal, H. Tagawa, and W. Lehnert, PV 97-40 (The Electrochemical Society Proceedings Series, Pennington, NJ 1997), p. 1021.
20. D.L. Meixner and R.A. Cutler, *Solid State Ionics*, **146**, 273 (2002).

21. D.L. Meixner and R.A. Cutler, *Solid State Ionics*, **146**, 285 (2002).
22. A.J. Bard and L.R. Faulkner, *Electrochemical Methods Fundamentals and Applications* (John Wiley and Sons, NY, NY, 1980), p. 91.
23. T. Ishihara, M. Higuchi, H. Furutani, T. Fukushima, H. Nishiguchi, and Y. Takita, *J. Electrochem. Soc.*, **5**, 144 (1997).
24. K. Huang, M. Feng, and J.B. Goodenough, *J. Am. Cer. Soc.*, **79**, 4 (1996).
25. K. Huang and J. Goodenough, Final Report to EPRI, Report No. TR-108742, Oct. 1997.
26. J.W. Yan, Z.G. Lu, Y. Jiang, Y.L. Dong, C.Y. Yu, and W.Z. Li, *J. Electrochem. Soc.* **149**(9), A1132 (2002).
27. S. Balagopal, I. Bay, and S. Elangovan, in *Proc. Fifth European SOFC Forum* (2002), p. 233.
28. U.S. Patent 6,265,095—Interconnect for Solid Oxide Fuel Cells.
29. E. Batawi, W. Glatz, W. Kraussler, M. Janousek, B. Doggwiler, and R. Diethelm, in *Proc. SOFC VI, Electrochem. Soc.*, edited by S.C. Singhal and M. Dokiya, 99–19, Honolulu, HI (1999), vol. 99–11, p. 731.
30. V.E. Stein and R.E. Richards, 7th Clean Coal Technology Conference, June 21, 1999.
31. V.E. Stein and R.E. Richards, 16th *International Pittsburgh Coal Conference*, Oct. 11, 1999.
32. D. Khang, et al. U.S. Patent 5516359, 1996.
33. R.M. Thorogood, et al., U.S. Patent 5240480, 1993.
34. S.L. Russek et al., U.S. Patent 5562754, 1996.
35. S.L. Russek et al., U.S. Patent 5565017, 1996.
36. D. Khang, et al., U.S. Patent 5657624, 1997.
37. M.F. Carolan, C.M. Chen, and S.W. Rynders, ACS Spring Meeting, New Orleans, LA, USA, March 26, 2003.
38. S. Nataraj, R.B. Moore, and S.L. Russek, U.S. Patent 6048472, 2000.
39. S. Nataraj and S.L. Russek, U.S. Patent 6077323, 2000.
40. S. Nataraj and S.L. Russek, U.S. Patent 6110979, 2000.
41. S. Nataraj, P.N. Dyer, and S.L. Russek, U.S. Patent 6114400, 2000.