

DoE award number: DE-FG02-95EW12610

Recipient: Universidad del Turabo, Sistema Universitario Ana G. Méndez, Inc. (SUAGM)

Project Title: DoE Chair of Excellence in Environmental Disciplines

Principal Investigator: Dr. Dennis Alicea, September 1995 to April 2005

Dr. Roberto Loran, May 2005 to September 2011

Final Technical Report for the period September 29, 1995 – September 29, 2011

Executive Summary

This report summarizes the activities performed under the contract DE-FG02-95EW12610 during the period of September 29, 1995 to September 29, 2010, and a no-cost extension from September 30, 2010 to September 29, 2011.

The initial proposal approved had as the main objectives of the program the development of academic programs in the Environmental Sciences and Engineering, and Research and Development focused in the initial works on environmentally friendly processes and later revised and expanded to include: (1) renewable energy, (2) environmentally friendly processes, and (3) international cooperation.

In 2006, the Massie Chair of Excellence Program was moved to the National Nuclear Security Agency, National Nuclear Security Administration (NNSA) and the Office of Defense Nuclear Non-Proliferation (DNN) and DoE required the project to submit a revised proposal aligned with the priorities of the Administration. The main objectives of the revised program included: (1) Research – (a) investigative research of the properties and potential applications of extremely high surface area silica materials as low refractive index and high transparency aerogel silica for Cherenkov Counters, (b) Investigative Study of Magnetic and Electronic Transport Properties at Material Interface in Magnetic Heterostructures using Gd ; (2) Student Development: develop an interest in research activities that promote the involvement of minority undergraduate and graduate students through work on research teams, internships, conferences, new courses; and, (3) Support -: (a) Research Administration and (b) Dissemination through international conferences, the development of the UT Distinguished Lecturer Series on Sciences, Technology and Engineering and presentations at the annual Universidad del Turabo (UT) Researchers Conference.

Dr. Dennis Alicea, Chancellor of Universidad del Turabo (UT), was the initial Principal Investigator from 1995 to April 2005 and Dr. Sastry Kuruganty as the Faculty Chair of the Program for the period of 1996-2000. In August 2000, Dr. Kuruganty left the Massie Chair position and continued as a professor in electrical engineering at UT. The work of the Massie Chair Program continued to be carried out under the School of Engineering. Also an extensive search was carried out for several years in which potential candidates international and local candidates were interviewed to fill the faculty chair. After having selected an appropriate candidate the required visa that was worked on for over a year was not approved. In May 2005, under the approval of DoE, Dr. Roberto Lorán was appointed PI and Chair. and held this appointment throughout the duration of the rest of the grant that finalized after a no cost extension period on September 29, 2011.

The following technical report demonstrates that the activities proposed, and approved changes by DoE in strategies or focus under the grant, were carried out and proposed outcomes achieved. The

document is organized in three parts. Period 1 of the report summarizes the activities performed during the initial period lead by Drs. Alicea and Kuruganty September 1995 to April 2005; and, Period 2, Components I and II the activities performed under the leadership of Dr. Lorán as PI and Chair in the period from May 2005 to September 2011.: 1. **Research Activities**, and 2. **Student Development and Support**. Period 2, Component II also includes a summary of activities relating to the general scope of the Massie Chair Program at Universidad del Turabo.

Period 1: September 1995 to April 2005 (Dr. Dennis Alicea, PI; Dr. Sastry Kuruganty, Faculty Chair) Focus: Environmental Consciousness and Academic Programs

The search to fill the Massie Chair of Excellence faculty position began in September 1995 culminating in the appointment of Dr. Sastry Kuruganty in September 1996. He served as the faculty chair until July of 2000. Dr, Dennis Alicea was the Principal Investigator for the program from September 1995- May 2005.

The work of the Massie Chair during this period included, leading the establishment of the new undergraduate program in electrical engineering at the School of Engineering until completion, working on compliance of requirements to achieve ABET accreditation of the young School of Engineering B.S. Mechanical Engineering and B.S. Electrical Engineering programs, mentoring junior faculty, teaching undergraduate courses in electrical engineering and developing a research program in environmentally conscious manufacturing. During the period of 1996 to 2000, the electrical engineering curriculum was revised. The School of Engineering undergraduate laboratories were designed and developed and efforts were focused towards fulfilling the requirements to be able to seek ABET accreditation.

The main focus of the Massie Chair work from 1995 to 2005 was on curriculum and infrastructure development of the School of Engineering and support to the development of environmental science programs in the School of Science and Technology. Concentrated efforts were focused on fulfilling requirements to be able to achieve ABET accreditation of the School's programs and establishing working relationships with private industry and the governmental sectors.

In 1998, scientific papers were presented at two well-known national conferences:

- 1) "A Computer Integrated Electromechanical Energy Conversion Laboratory for the COINAR Conference, Interamerican University, San Juan, Puerto Rico, March 27 1998
- 2) "Impact of Diversity Exchange on the Reliability of a Power System" at the 30th Frontiers of Power Conference, Oklahoma State University. Stillwater, Oklahoma, October 1998

Several proposals were submitted for research funding and laboratory development during this period, including among others the following approved proposals:

1. "A Proposal for Environmental Engineering Curriculum Development and Environmentally Conscious Manufacturing Research for Hispanic Bilingual Program at Turabo University", DOE EM (\$150,000)
2. "A Proposal for Microwave and RF Laboratory Equipment", AFOSR DOD (\$171,663)

3. "Bridging the Massie Chair Program in Environmental Engineering and the National Hispanic Bilingual Program", DOE EM (\$320,000).

Through the efforts of the School of Engineering and the Massie Chair Program, the Mechanical Engineering and the Electrical Engineering programs were accredited by ABET in 2006

An extensive search, from July 2000 to April 2005, was carried out for a new professor to occupy the Massie Chair position that had the required credentials and expertise in the areas of interest for development of the Massie Chair program and the School of Engineering. This took place through international professional publications, newspapers, professional conferences and other means. Several candidates international and local through the evaluation process, some were considered appropriate for the position; however, they finally decided not to accept the position due to problems with visa, geographic location, other offers, among others.

Period 2: May 2005- September 2006 Environmental Consciousness and Academic Programs

September 2006 – September 2001 Revised approved proposal Nuclear Non Proliferation and Stewardship

Dr. Roberto Lorán PI and Massie Chair

In May 2005, Dr. Roberto Loran was appointed as the Massie Chair, with the approval of DoE, and served in this capacity for the duration of the grant that closed in September 2011.

Work was continued under the objectives of the original approved proposal: development of academic programs in the Environmental Sciences and Engineering, and Research and Development focused in the initial works on environmentally friendly processes and later revised and expanded to include: (1) renewable energy, (2) environmentally friendly processes, and (3) international cooperation.

Upon the instruction of DoE it was necessary to revise the original focus of work of the approved proposal and transition to a Nuclear Non Proliferation and Stewardship focus. This took considerable work and effort in 2006. The new objectives of the Massie Chair of Excellence of UT were revised to the following:

The main objectives of the revised program included: (1) Research – (a) investigative research of the properties and potential applications of extremely high surface area silica materials as low refractive index and high transparency aerogel silica for Cherenkov Counters, (b) Investigative Study of Magnetic and Electronic Transport Properties at Material Interface in Magnetic Heterostructures using Gd ; (2) Student Development: develop an interest in research activities that promotes the involvement of minority undergraduate and graduate students through work on research teams, internships, conferences, new courses; and, (3) Support -: (a) Research Administration and (b) Dissemination through international conferences, the development of the UT Distinguished Lecturers Series on Sciences, Technology and Engineering and presentations at the annual Universidad del Turabo (UT) Researchers Conference.

The following provides the technical information that demonstrates that the activities proposed under the original proposal and the revised proposal in this period were carried out and the outcomes accomplished as proposed.

Component I: Research Activities

During the period of May 2005 to September 2006 following research activity relating to Environmentally friendly processes was carried out and successfully completed.

Sub project: Research and development of new perovskite-alumina hydrogen permeable asymmetrical nanostructured membranes for hydrogen purification, and extremely high specific surface area silica materials for hydrogen storage in the form of ammonia

Dr. Rolando Roque-Malherbe Subproject PI, Dr. Santander Nieto and Mr. Will Gómez Research Assistants

Accomplished Tasks 2005 -2006

In September 2005, Dr. Rolando Roque-Malherbe was hired as Senior Researcher of the program. Two (2) fulltime postdoctoral research assistants were incorporated to the team partially funded by the grant: Dr. Santander Nieto (Chemical-physicist) and Mr. Will Gómez (chemical-physicist). In addition, four (4) undergraduate students were trained and hired as Laboratory Assistants. The research group efforts were concentrated in hydrogen technologies, specifically in the development of new perovskite-alumina hydrogen permeable asymmetrical nanostructured membranes for hydrogen purification, and extremely high specific surface area silica materials for hydrogen storage in the form of ammonia.

The Hydrogen Technology Laboratory was equipped: Spin Processor, Box Furnace, and a Q500 Thermogravimetric Analyzer were purchased, installed and calibrated.

The research efforts were funded by the Massie Chair Program and UT internal funds. Supplementary funding to expand the research were sought through a proposal entitled "Ammonia Adsorption on Nanostructures Silica Materials for Hydrogen Storage and other Applications" submitted in January 2006 to DoD-ARO-IRS-HIS but not funded. A joint proposal with Tennessee University entitled "Ammonia Adsorption on Nanostructures Silica Materials for Hydrogen Storage" was submitted in July, 2006 to NOETL.

Process for heavy metal removal from waste water. Patent registration #34,554. 2006-2007

After the approval by DOE of the revised proposal in September 2006, the contribution of the UT DSPMCoE team research efforts were directed toward increasing knowledge in chemical and materials analysis (subproject 1) and magnetic multilayered structure development relevant to nuclear processes and technology (subproject 2) which has been demonstrated by nineteen (19) publications, (including 3 books), five (5) presentations and three (3) international conferences abstracts.

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Sub-Project 1: Synthesis and Characterization of low Refractive Index Aerogel Silica for Cherenkov Counters- Dr. Rolando Roque-Malherbe Sub-project PI, Dr. Jose Duconge Sub-project Co-PI, Dr. Santander Nieto Assistant Researcher, Francisco Diaz and Carlos Neira Associate Researchers.

I. Introduction

The goals of the "Synthesis and Characterization of Low Refractive Index Aerogel Silica for

Cherenkov Counters” project were to: (1) carry out a research project that would have an innovative effect on the mission and goals of the DOE by helping to meet the specific science needs of the Defense Nuclear Nonproliferation Program in the topics of Chemical and Materials Analyses for Nuclear Processes and Technology, specifically in the Synthesis and Characterization of Materials that are Applicable to Nuclear Technology and Particle Analyses and Factors that Influence Particle Formation. Also the research project relates to the topic of Radiation Detection/Sensing, specifically the Development of Radiation Detection Materials, by conducting an innovative R&D project with impact on the Nuclear Program; (2) develop a multidisciplinary R&D and a minority undergraduate students research training program that promoted the fusion of Physics, Chemistry and Technology; and, (3) collaborated with universities, industry, and other government agencies while expanding the research infrastructure and faculty research productivity in minority Hispanic Serving Institutions (HSI). The research aim of the proposed research project was to investigate the properties and potential applications of extremely high surface area silica materials as low refractive index and high transparency aerogel silica for Cherenkov counters. The main objectives of the project can be summarized as follows:

- Optimization of the synthesis procedures to improve the low refractive index and transparency capability of nanostructured silica extremely high specific surface area aerogel materials.
- Characterization of the obtained materials with SEM, TGA and FTIR
- Study of the silica surface area and porosity with N₂ adsorption at 77 K
- Study of the refraction index
- Study of the transparency of the obtained materials.
- Training of one (1) graduate student and two (2) undergraduate minority students in the synthesis, and characterization of aerogel silica.

The starting point for the present research project were silica particle-packing materials, which exhibited a very high specific surface area, obtained by the Institute of Chemical and Biological Technology research team [1-4] at Universidad del Turabo (UT). UT researchers have obtained silica nanostructured materials showing extremely high specific surface area, i.e., up to 2,200 m²/g [1-4]. It was anticipated that these materials, which were obtained as xerogels if are produced as aerogels would have a very low refraction index and very high transparency. Summarizing, the principal objectives of this sub project was to develop and demonstrate novel multidisciplinary technologies that would enhance the operability and maximize the performance of low refractive index and high transparency aerogel silica for Cherenkov counters. In addition, students were exposed to the use of these materials in the construction of Cherenkov Counters.

I. Accomplished tasks 2006-2007

Task 1. Helix Supercritical Dryer Provided by Applied Separations (930 Hamilton Street Allentown, PA 18101. Phone: 610-770-0900) Acquisition

Aerogels are one of the different forms of amorphous silica which were obtained by the sol-gel method. Sol-gel processing specifies a type of solid materials synthesis method, performed in a liquid, and at low temperature. The produced inorganic solids, mostly oxides or hydroxides, are formed by chemical transformation of chemical solutes termed precursors. Aerogels are dried gels synthesized by traditional sol-gel chemistry, but dried, by supercritical drying. As a result, the dry samples keep the porous texture, which they are in the wet stage. The silica gels were then prepared by a sol-gel process using tetraethyl orthosilicate (TEOS). This process produced a silica gel skeleton in ethanol or methanol. The alcohol was subsequently removed by placing the wet gel in a supercritical dryer.

The silica gel rods were placed in a vessel included in an autoclave; then, the autoclave was pressurized to 5-6 MPa with CO_2 and cooled from 300 K to 278-283 K. Liquid CO_2 ; then, flushed through the vessel until all the alcohol was removed from within the silica gel and the autoclave vessel. After the gels were liberated of the alcohol, the vessel was heated up to 308 K. Thereafter, CO_2 was released to keep up a pressure slightly above the critical pressure of CO_2 , a pressure of about 8 MPa. The system is maintained in this state for a time-span depending on the thickness of the gel.

The construction of the Helix Supercritical Dryer was contracted by us on October, 2006. However, it was delivered to Universidad del Turabo, during August, 2007. It was delivered without any instructions to be put together. It was necessary to contact the supplier in order to have a service engineer sent to put together the equipment. The supplier was very slow in this entire process causing delays in research developments as the use of this equipment was unavoidable, in order to get the aerogel. Considerable work was put in to resolve this situation as soon as possible.

Task 2. Silica Synthesis

The batch preparation to synthesize the silica gel was the following:

- Alcohol + catalysts (base) + DDW (if needed) (mixed with strong agitation)
- TEOS was added to the reaction mixture
- The mixture was stirred at room temperature for 1.5 hours
- After the first step of the synthetic procedure the product was dried.

In order to carry out this task in October 2006 the necessary chemicals, ethanols, methanol, TEOS, triethylamine (TEA), ammonium hydroxide, hydrofluoric acid were acquired to clean the vessels, as well as other necessary chemicals. The chemicals were delivered in February 2007. The researchers were then trained in the synthesis process. However, it was impossible to achieve the aerogel as we did not have yet the supercritical dryer in operational conditions.

In addition, heaters, rotors, and some teflon vessels were acquired in order to carry out the synthesis process; as well as the necessary protection devices to manipulate the synthesis safely.

Task 3. Characterization

Scanning Electron Microscopy (SEM). The necessary contacts were made to use the scanning electron microscope located in the Cayey UPR Campus. Besides, the researchers were trained in the theory and practice of scanning electron microscopy.

Thermal Gravimetric Analysis (TGA). The TA Q-500 TG equipment went through extensive maintenance in order to optimize its performance for the production of the aerogel sample.

Fourier Transform Infrared (FTIR) spectrometry. The Bruker FTIR confronted a problem with the semitransparent mirror. One of the research group members detected this problem during the maintenance of the equipment. The mirror was purchased with institutional funds obtained from the School of Science to be used for this purpose. A dry air generator was installed in order to avoid the destruction of the mirror. In addition, the researchers were trained in the theory and practice of IR spectrometry.

Refractive Index Measurement. A device was constructed in our laboratory to measure the refractive index (n) of the aerogel material, with the help of the method of minimum deflection. The following equation was applied:

$$n = \frac{\sin\left(\frac{\gamma + \beta}{2}\right)}{\sin\left(\frac{\gamma}{2}\right)}$$

Where, γ , is the apex angle of the aerogel prism corner used for the measurement, and, β , is the minimum deflection angle (see Fig. 1).

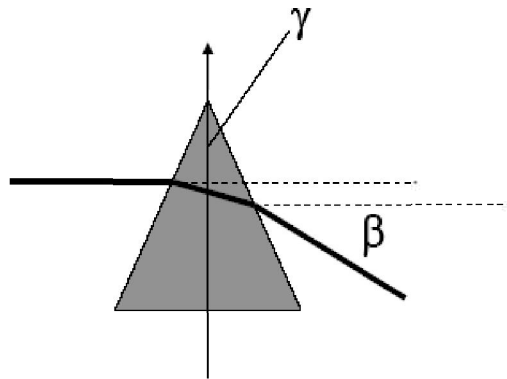


Fig. 1. Geometry of the arrange for the measurement of the refractive index

The test prism was placed in a PASCO rotation sensor coupled with the PASCO interface to a computer in order to measure the angle, β . The measurements were been performed with an He-Ne laser at 633 nm. The precision and the accuracy of the method was appropriate for the purpose.

Transmittance Measurement. The transmittance of the produced aerogels was measured, when obtained, with the help of a UV Shimadzu Spectrophotometer. The transmittance, $\frac{T}{T_0}$, was defined by the following relation:

$$\frac{T}{T_0} = \exp\left(-\frac{d}{\Lambda}\right)$$

Where, d , is the aerogel sample thickness and, Λ , is the transmission length. The researchers were trained in the operation of the UV equipment.

Adsorption Study. Gas and vapor adsorption is a powerful means to study porous materials. In order to measure the specific and external surface area and the pore volume with the help of the adsorption study, the adsorption isotherms of N_2 at 77 K of the aerogel samples previously degassed at 250°C during seven hours in high vacuum (10^{-6} Torr) was obtained in an Autosorb-1, Automatic Physisorption Analyzer. The operational capability of the Autosorb-1 was radically improved with institutional funds obtained by the Institute of Physical Chemical Research to be used for this purpose. In addition, the researchers were trained in the theory and practice of adsorption of gases and vapors in solids.

Students Participation.

The students that participated in the project were been directly involved in all the above described process for the characterization of the produced materials using the above described modern materials research methods.

Task. 4. Seminars.

Group seminars were delivered every Friday at 3.00 PM. In these seminars the members of the group were informed regarding the theory and practice of: scanning electron microscopy, infrared spectrometry and adsorption. In addition, topics were studied related to the theory of X-ray diffraction, the Rietveld method, the theory of diffusion and the structure of materials.

II. Accomplished Tasks 2007-2008

Task 1. Helix Supercritical Dryer Installation and Running:

1. A basket was designed (Fig. 1) that was filled with templates with the form of a prism (Fig. 2) and a slit (Fig. 3) in order to dry the gel with these geometries and to make the required measurements. The prism was used for the refraction index measurement, and the slit for the transparency measurement.

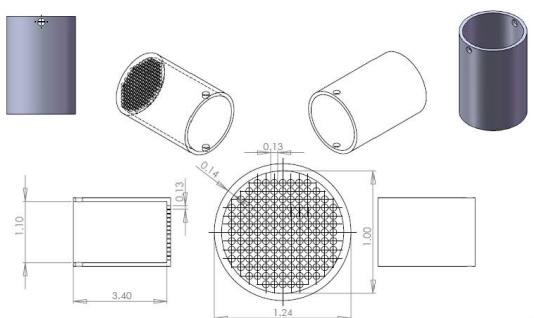


Fig. 1.



Fig. 2a.

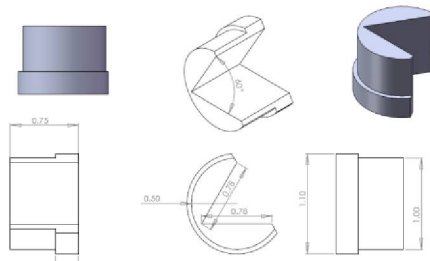


Fig. 2b



Fig. 3a.

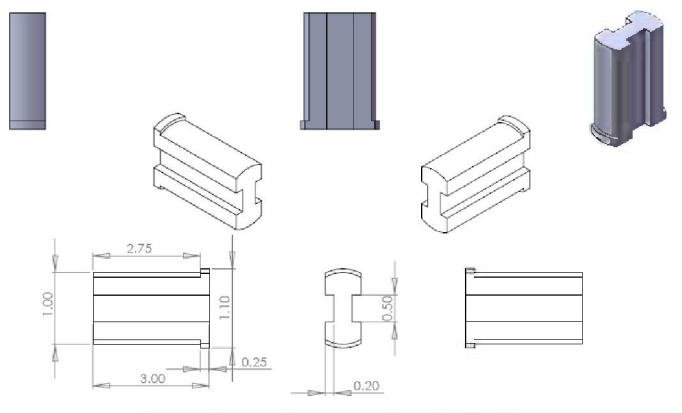


Fig. 3b

2. The basket drawings were submitted to Applied Separations for fabrication; however, this company never proceeded to construct these parts, notwithstanding the fact that they promised to make them. Due to the delay produced by the lack of this basket, the PI of the project decided to carry out other tasks in order to make use of the research time. These efforts consisted in, using a very small part of the resources provided by the DOE for this project to carry out two research projects.

3. One of the project was the "Mechanocatalytic Decomposition of Phenol" carried out by: R. Roque-Malherbe, M. C. Cotto, S. Nieto and J. Duconge. In this study TiO_2 (rutile) powders characterized by XRD and SEM were used as catalyst in the mechanocatalytic decomposition of phenol. To investigate this mechanical activation process: 100 mg/l phenol aqueous solutions were ball milled by: 0, 12, 24, 48 and 72 h without and with the catalyst, and analyzed with UV spectrometry reaction products. When the catalyst was not included in the process, phenol was not affected by the milling process. However, when the catalyst was included in the process phenol was decomposed, following the first order kinetics. The stability of the catalyst during the process was tested by the analysis of the XRD profiles of the catalysts milled by: 0, 24, 48 and 72 h. This study did not show any evidence of change in the XRD profiles. As a result it, it was shown that the mechanical activation of rutile powders decompose phenol as a photocatalyst when it is irradiated with UV light, or as a sonocatalyst when irradiated with ultrasound waves. As far as we know this is a new catalytic process. This paper was presented in the IUPAC-XXVIII Latin American Congress of Chemistry.

4. The other study was: "Paranitrophenol Liquid-Phase Adsorption in Dealuminated Y Zeolite" by: C. Muñiz-Lopez, J. Duconge and R. Roque-Malherbe. In this research we have studied the liquid-phase paranitrophenol (PNP) dynamic adsorption in a packed bed adsorption reactor (PBAR), filled with dealuminated Y zeolite (DAY) and granulated active carbon (GAC). In addition, was obtained the liquid-phase adsorption isotherm for the system: PNP in aqueous solution-DAY zeolite, at 300 K. The

DAY zeolite and the GAC were characterized with: adsorption methods. Besides, the DAY was, also, characterized with: XRD, SEM and EDAX. Some of the operational parameters which characterize the performance of the PBAR filled with both adsorbents were calculated. To evaluate these results, was considered the breakthrough experiment as a frontal analysis chromatographic event and were applied the DeVault and van Deemter equations. Besides the equilibrium adsorption data was fitted to the Langmuir isotherm. It was concluded that the reactor filled with the DAY zeolite operates more efficiently than those filled with the GAC, because of the stronger adsorbate-adsorbent interaction in the case of the DAY zeolite. The paper was published by the Journal of Colloid and Interface Science and was presented in the IUPAC-XXVIII Latin American Congress of Chemistry.

5. The research group decided to construct by ourselves the basket that Applied Separations did not produce. The PI delayed this decision as the supercritical drying facility works at 10 MPa, that is 100 atmospheres, consequently it was dangerous to introduce a modification. However, the PI studied the problem with our service technician and constructed this part and tested it safely. In Fig. 4 is shown a photo of the constructed cylindrical template (see 1 and 2) and the basket (see 3). We changed the geometry of the template to a cylindrical one in order to simplify the construction.

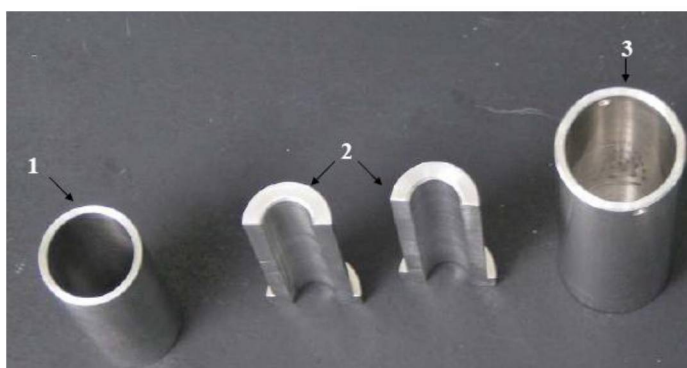


Fig. 4. Cylindrical Template (1 and 2) and Basket (3).

In Fig. 5 is a photo illustrating the procedure to introduce the basket in the supercritical dryer with the help of a hanger constructed for this purpose



Fig. 5. Introduction of the Basket with the Cylindrical Template Inside the Supercritical Dryer.

Task 2. Silica Synthesis

In this task the silica gels were prepared by a sol-gel process using tetraethyl orthosilicate (TEOS) and other methods were also tested. This process produced a silica gel skeleton in ethanol or methanol. The alcohol was subsequently removed by placing the wet gel in a supercritical dryer. The silica gel rods were placed in a vessel included in an autoclave; then, the autoclave was pressurized to 5-6 MPa with CO_2 and cooled from 300 K to 278-283 K. Liquid CO_2 ; then, flushed through the vessel until all the alcohol was removed from within the silica gel and the autoclave vessel. After the gels were liberated of the alcohol, the vessel was heated up to 308 K. Thereafter CO_2 was released to keep up a pressure slightly above the critical pressure of CO_2 that was a pressure about 8 MPa. The system was maintained in this state for a time-span depending on the thickness of the gel. The batch preparation to synthesize the silica gel was as follows:

- Alcohol + catalysts (base) + DDW (if needed) (mixed with strong agitation)
- TEOS was added to the reaction mixture
- The mixture was stirred at room temperature for 1.5 hours
- The gel was aged during 1 to 5 days
- After the aging step of the synthetic procedure the product was dried

1

During this period the synthesis and aging processes was mastered in order to get a real gel to be dried. Trying the following compositions (see Table 1):

Table 1. Batch composition for the silica synthesis by means of the hydrolysis of TEOS in ethanol and methanol in the presence of an amine.

Sample	TEOS [ml]	DDW [ml]	NH ₄ OH [ml]	Amine [ml]	MeOH [ml]	EtOH [ml]	T [°K]
70bs2	0.25	0	0	2.0	0	10	300
79bs2	0.45	0	0	2.5	0	10	300
68bs1	0.25	0	0	1.0	10	0	300

We then aged the produced gel by different methods, as the aging process is very important for the subsequent drying process. The aging procedures were the following:

1. with the beaker containing the gel completely open,
2. with the beaker containing the gel partially open
3. with the beaker containing the gel completely covered with a paraffin film

The aging times were: 0, 12, 18, 24, 48 and 72 h. and one sample aged by five months. The aged samples were supercritically dried without thermal drying and thermally dried at 50 and 70 °C by 2 h. Thereafter, the aged gels were supercritically dried as follows: first the gel was flowed liquid CO₂ at 7 MPa at 298 K during 2 h; later pressure was raised up to 10 MPa at 298 K. Then, the temperature was raised up to 313 K at 10 MPa. In this condition the process was carried out during 6, 12, 24, 36, h.

The gel could be as well dried in a furnace to get a xerogel which has other applications. We have applied this xerogel in hydrogen storage. In this regard the following paper was accepted for publication: R. Roque-Malherbe, F. Marquez, W. del Valle and M. Thommes, Ammonia Adsorption on Nanoporous Silica Materials for Hydrogen Storage and Other Applications, *Journal of Nanoscience and Nanotechnology* 8 (2008). A poster was also presented at the International Symposium on Molecular Materials, MOLMAT 2008, that was held in Toulouse France, in July 2008, by: R. Roque-Malherbe and F. Marquez-Linares, Synthesis and Characterization of High Specific Surface Area Nanostructured Silica Materials for Hydrogen Storage and Other Applications.

Task 3. Characterization

Adsorption Study: The contract for the maintenance of the Autosorb- was signed by the provider on April 2008. The repairs of the Autosorb-1 were carried out from June 23 to June 26, 2008. This upholding consisted in the installation of a new dry pump, repair of the turbomolecular pump, change of the vacuum seals, cleaning and improvement of the gaskets, a complete calibration of the volumetric device and the test of silica samples. The operational capability of the Autosorb-1 was radically improved with this maintenance which was pay for with institutional funds. The two xerogel samples produced with the methodology previously mentioned were studied with the autosorb-1.

III. Accomplished Tasks 2008-2009

Task 1. Supercritical Drying

The basket to be filled with templates with the form of a prism and a slit to dry the gel with these geometries was never produced by Applied Separations, however, we constructed it by ourselves. In Fig. 1 a photo of the constructed cylindrical template (see Fig 1) and the basket (see Fig. 1). We have changed the geometry of the template to a cylindrical one in order to simplify the construction.



Fig. 1. Cylindrical Template (1 and 2) and Basket (3).

In Fig. 2 is shown a photo illustrating the procedure to introduce the basket in the supercritical dryer with the help of a hanger constructed for this purpose



Fig. 2. Introduction of the Basket with the Cylindrical Template Inside the Supercritical Dryer.

A heavy duty weighing machine was purchase in order to control the amount of CO₂ remaining in the cylinders which fed the supercritical dryer. This machine is needed to carry out long experiments, because a lack of CO₂ in the cylinders could damage the supercritical dryer.

Some 60 different silica gel synthesis procedures were carried out, from this one that was supercritically dried. During the next drying process the supercritical drying machine faulted, due to the breakdown of a high pressure seal. It was repaired and then using the baskets constructed by the research team the equipment was tested and set up to carry out the silica gel supercritical drying process. In addition some 10 different silica gel synthesis procedures were carried ot, with a procedure different from those previously carried out (see below). Of these five were supercritically were dried.

Task 2. Aerogel Silica Synthesis

The first process applied to achieve the silica gels was a sol-gel process using tetraethyl orthosilicate (TEOS) [1-8]. This process produced a silica gel skeleton in ethanol or methanol. The alcohol was subsequently removed by placing the wet gel in a furnace or a, to achieve a xerogel or in a supercritical dryer, to get an aerogel. For the synthesis of the silica gel with this procedure variations of the following compositions were used (see Table 1):

Table 1. Batch composition for the silica synthesis by means of the hydrolysis of TEOS in ethanol and methanol in the presence of an amine

Sample	TEOS [ml]	DDW [ml]	NH ₄ OH [ml]	Amine [ml]	MeOH [ml]	EtOH [ml]	T [°K]
70bs2	0.25	0	0	2.0	0	10	300
79bs2	0.45	0	0	2.5	0	10	300
68bs1	0.25	0	0	1.0	10	0	300

The batch preparation was as follows [1-8]:

- The alcohol + the catalysts (base) + DDW (if needed) were mixed with strong agitation
- TEOS was added
- The mixture was intensively stirred at room temperature for 1.5 hours.
- The product was dried to get xerogels (thermal drying) or aerogels (supercritical drying).

Thereafter we aged the produced gel by different methods, since the aging process is very important for the subsequent drying process. The aging procedures were the following:

- with the beaker containing the gel completely open,
- with the beaker containing the gel partially open
- with the beaker containing the gel completely covered with a paraffin film

The aging times were 0, 12, 18, 24, 48 and 72 h. and one sample was even aged by five months. The aged samples were thermally dried at 50 and 70 °C by 2 h to get xerogels. Two samples aged at 48 and 72 h gels were supercritically dried as follows: first the gel was flowed liquid CO₂ at 7 MPa at 298 K during 2 h; later pressure was raised up to 10 MPa at 298 K. Then, the temperature was raised up to 313 K at 10 MPa. In this condition the process was carried out during 12 h.

The previous methodology provides good xerogels but not very good aerogels consequently was tried a new synthesis methodology. With this methodology were synthesized five different silica gel samples. The synthesis procedure was different as those applied previously [1-8]. The batch preparations were as follows [9,10]:

- Ethanol (70 ml) + DDW (140 ml) + 30% aqueous ammonia solution (0.55 ml) 0.5 M ammonium fluoride solution (2.4 ml) were mixed with agitation
- TEOS (100 ml) + ethanol (80 ml) were also mixed
- The solution number 1 was gradually added to solution number two and the mixture was intensively stirred at room temperature for 0.5 hour
- The products were aged at 300 °K, during: 14, 21, 22, 23 and 28 days.

The gels aged during, 14, 21, 22 and 23 days were supercritically dried to get four aerogel samples. The procedure applied to get the aerogels was the following:

- The samples were flushed three times with liquid CO₂ at 100 Bar and 300 K during 3 hour each flush

- Thereafter the temperature was increased up to 313 K and at the same pressure the samples were flushed with gaseous CO₂ at 100 Bar during: 12, 24 and 36 hours for the samples aged by 21, 22 and 23 days. The sample aged by 14 days was flushed during 6 hours

Task 3. Characterization with Thermogravimetric Analysis.

The thermogravimetric analyzer TA TQ-500 was applied in the characterization of the different samples produced. Ten different samples: three xerogels, one aerogel, one carbon nanotube, three molecular organic frameworks, two zeolites and one active carbon were analyzed during the year. As follows is the report of the results which are more closely related with the project which is one of the aerogel samples, i.e. those aged by 21 days. The result displayed in Fig. 3, shows that the produced sample did not contain a large amount of water. Consequently the tested sample did not show a high dipolar interaction with the water molecule [2.3].

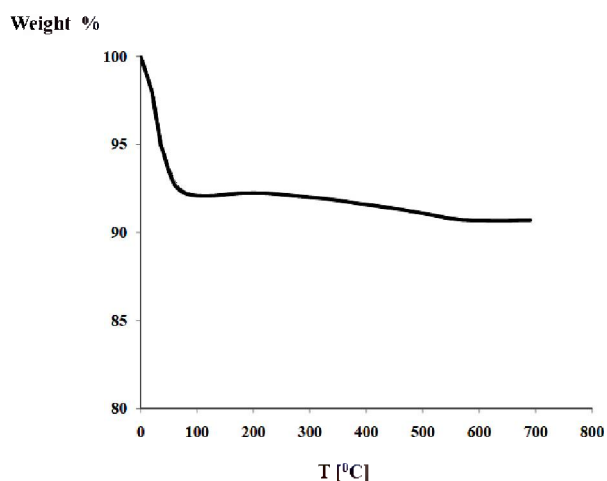


Fig. 3. TGA profile of the silica aerogel sample aged during 21 days.

Task 4. Adsorption Study.

The maintenance of the Autosorb-1 was carried out in June, 2008, with institutional funding. The maintenance consisted in the installation of a new dry pump, repair of the turbomolecular pump, change of the vacuum seals, cleaning and improvement of the gaskets, a complete calibration of the volumetric device and the test of silica samples.

Five xerogels and one aerogel with this equipment were studied. In addition, one carbon nanotube, three molecular organic frameworks, two zeolites, one active carbons, and three semiconductor catalysts, such as rutile, anatase and zinc oxide, between other samples were studied.

In the present report the details of only one of the studied aerogels studied. The automatic surface and porosity analyzer Quantachrome Instruments AS-1, was applied in the study of the obtained

aerogel silica sample. a very detailed adsorption isotherm of N_2 at 77 K in the aerogel aged by 21 days was obtained (see Fig. 4) [2,3].

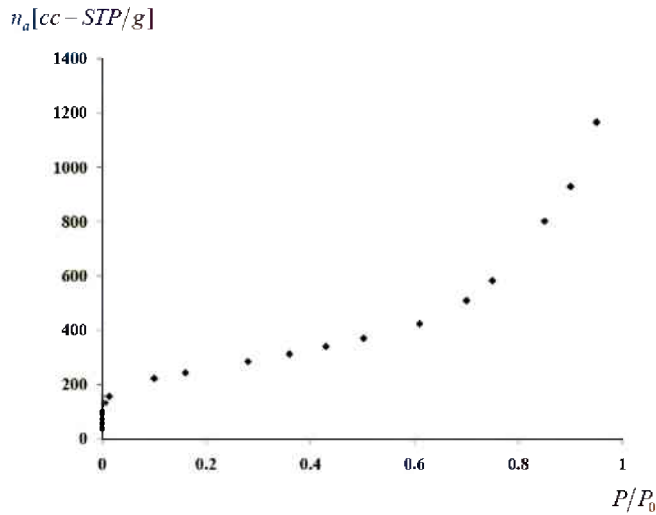


Fig. 4. Adsorption Isotherm of N_2 at 77 K in the aerogel aged by 21 days

This sample showed a very large specific surface area, specifically: $S = 1000 \text{ m}^2/\text{g}$, as is shown with the help of the BET plot (see Fig. 5) [3].

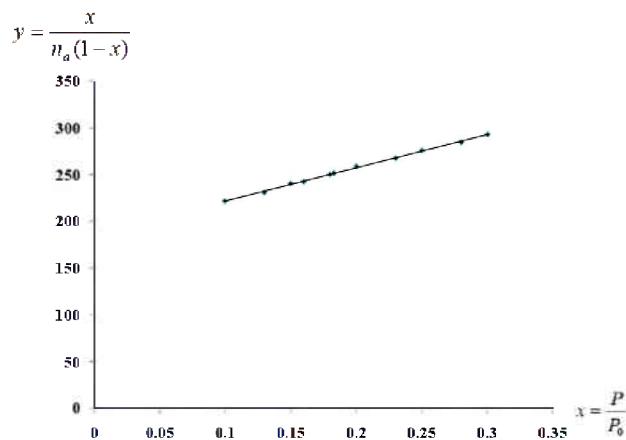


Fig. 5. BET Plot

This sample also showed a developed microporosity, as is shown by the Dubinin plot (Fig. 6) [3] and the Saito-Foley micropore size distribution (Fig. 7) [2], i.e., the measured micropore volume is: $W = 0.38 \text{ cm}^3/\text{g}$ and the micropore size is between 4-9 Å.

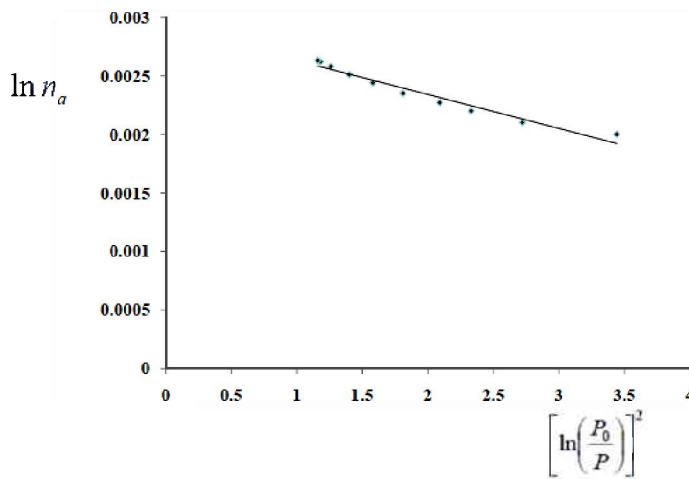


Fig. 6. Dubinin Plot

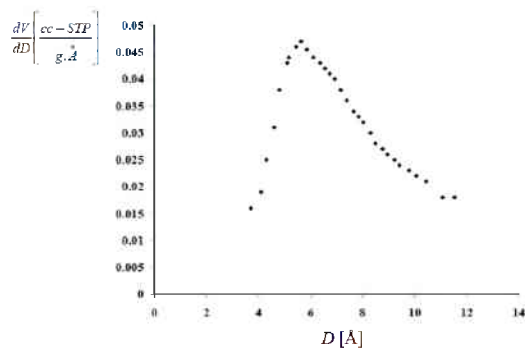


Fig. 7. Saito-Foley Pore Size Distribution

The sample also has a highly developed mesopore size distribution as is shown by the NLDFT pore size distribution (see Fig. 8) [3].

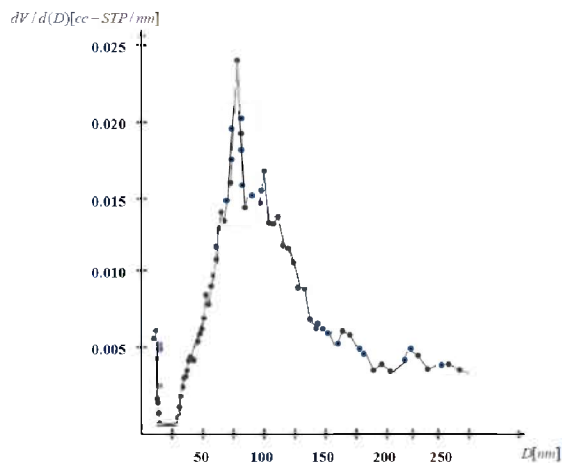


Fig. 8. NLDFT Pore Size Distribution

Concretely the total pore volume of the sample is $W_T = 1.7 \text{ cm}^3/\text{g}$ [3].

In addition, the sample aged during 21 days was submitted to Micromeritics, Atlanta, GA in order to make the ammonia adsorption isotherm at 300 K and up to 7 Bar in the automatic surface and porosity analyzer Micromeritics ASAP 2050. This study provided us an insight into the possible application of this sample for hydrogen storage as ammonia.

Task 5. Equipment Construction

i. CVD and Vacuum Facilities

A Chemical Vapor Deposition (CVD) facility was assembled. The equipment in the facility include a ceramic tube included in a furnace and a manifold comprising seven stopcocks and three gas flow meters to control the gas input into the heated quartz tube in order to carry out in this site the chemical vapor deposition processes. The facility can be used in different studies, for example in the production of carbon nanotubes.

Two vacuum lines were also assembled in order to give vacuum treatment to our samples and to also be able to study water adsorption.

ii. Dielectric Analysis of the Aerogel Samples

We had previously proposed to calculate the aerogel refraction index, n , with the help of the measurement of the aerogels relative permittivity. In order to carry out this measurement, at different frequencies, a parallel plate capacitor was constructed where a micrometer allows the adjustment of the parallel plate separation size (see Fig. 9), in order to accommodate the aerogel wafer sample [2,11-14]. The space between plates of this capacitor was filled with the aerogel.

Fig. 9. Circuit for the Measurement of the Parallel Plate Capacity.

The time dependence of any periodic function can always be expressed in terms of sine and cosine functions. In this sense, it is very convenient to apply the complex number representation, to express an alternate current (AC) using the following equation [2,11]:

$$V = V_0 e^{i\omega t} = V_0 (\cos \omega t + i \sin \omega t)$$

In which: ω , is the angular frequency. Evidently, the voltage of the alternate current is the real part of the above written equation.

In order to generalize the concept of resistance in alternate current (AC) circuits is defined the impedance as follows [2]:

$$\tilde{Z} = Z_r(\omega) + iZ_i(\omega)$$

Where, Z_r , is the real part of the complex number which represent the impedance, $i = \sqrt{-1}$ is the imaginary unit and, Z_i , is the imaginary part. This parameter is, normally, measured by the calculation of the ratio of the voltage response to the current perturbation which gives the impedance:

$$\tilde{Z}(\omega) = \frac{\tilde{V}(\omega, t)}{\tilde{I}(\omega, t)}$$

The study of materials by dielectric methods is carried out in alternating electric fields and the dielectric behavior is described, in a formal way, by the complex relative permittivity (or complex dielectric constant) [2,11]:

$$\tilde{\epsilon}(\omega) = (\epsilon_r'(\omega) - i\epsilon_r''(\omega))\epsilon_0$$

Where ϵ_0 , the permittivity of vacuum; $\epsilon_r'(\omega)$, is the real part of the complex relative permittivity (or real component of the complex dielectric constant) and $\epsilon_r''(\omega)$, the imaginary part of the complex relative permittivity (or imaginary component of the complex dielectric constant) [2,11-14].

It is possible to include in a single parameter the study of dielectrics generalizing the complex permittivity as follows [2]:

$$\tilde{\epsilon}_\sigma(\omega) = \epsilon_r'(\omega) - i \left(\epsilon_r''(\omega) + \frac{\sigma_0}{\omega \epsilon_0} \right)$$

In which: $\epsilon_r'(\omega)$ and $\epsilon_r''(\omega)$ are dielectric process, related by the Kramers-Kronig relations [2], if, Γ_σ , the direct current conductivity (d.c.), is negligible. It is necessary to assert, now, that the difference between: $\epsilon_r'(\omega)$ and $\epsilon_r''(\omega)$, and σ_0 have a very important physical meaning, inasmuch as the first two parameters are the result of finite displacements of charge (Polarization) and the third is the product of long range charge transport (conduction).

The relationship between the output (V_{out}) and input voltages (V_{in}) in the applied circuit (Figs. 9 and 10) is [2,11]:

$$V_{out} = -\frac{|Z_r|}{|Z_x|} V_{in} \quad (1)$$

Where: $|Z_r|$, is the complex impedance module of the equivalent circuit formed by the reference capacitor and $|Z_x|$, is the complex impedance module of the equivalent circuit formed by the capacitor filled with the aerogel sample under test

It is evident, that the explicit form for equation "1" is:

$$V_{out} = -\frac{\left[\left(\frac{1}{R_r} \right) + i(\omega C_r) \right]^{-1}}{\left[\left(\frac{1}{R_x} \right) + i(\omega C_x) \right]^{-1}} = -\frac{\left[(\omega C_x)^2 + \left(\frac{1}{R_x} \right)^2 \right]}{\left[(\omega C_r)^2 + \left(\frac{1}{R_r} \right)^2 \right]} V_{in} \quad (2)$$

Obtained with the help of the following expression:

$$\tilde{Z} = \frac{1}{\frac{1}{R} + i\omega C} \quad (3)$$

In which, the impedance of the resistance is: $Z_r = R$, and the impedance of the ideal capacitor is: $Z_c = 1/i\omega C$. Equation "3" describes the impedance of a resistance and a capacitor in parallel; where the reference and sample under test capacitors are connected in the circuit as real capacitors equivalent circuits (see Fig. 8) where: C_x , C_r and R_r , R_x are the respective capacitance and resistance of the capacitors filled with the aerogel sample "x" and the reference capacitor "r" (see Fig. 10).

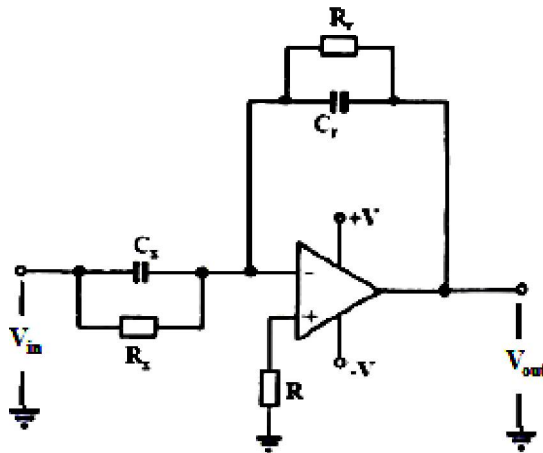


Fig. 10. Dielectric Sensor Circuit.

From equation "2", it is possible to show [2,11-13]:

$$V_{out} \approx \left[\frac{\epsilon_x'}{\epsilon_r'} \right] V_{in}$$

Our experiment was set up assuming: $1/R_r \approx 0$, and, $1/R_x \approx 0$, as the aerogel does not conduct electrons, and using the following relation: $C = \epsilon \cdot C_0$, where: C_0 , is the capacity of the empty capacitor and, ϵ_r' and, ϵ_x' , are the real parts of the complex relative permittivity of the reference and the powdered sample under test.

Consequently, the refraction index, n can be calculated with the help of the following expression:

$$n = \sqrt{\epsilon_r'}$$

Where, ϵ_r' , is the relative permittivity. Consequently, with the previously described method it was possible to measure the aerogel refraction index.

iii. Impedance Spectrometry

We have deeply studied impedance spectroscopy and made three tests in two different installations in order to apply this methodology to the characterization of the silica. Below (see Fig. 11) is shown a Nyquist plot of the test of solid electrolyte battery [2].

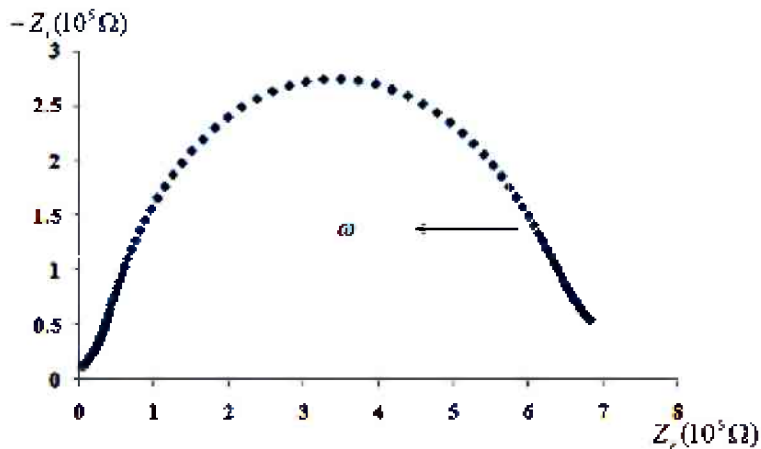


Fig. 11. Nyquist Plots (100 Hz to 1 MHz) of the Impedance Spectroscopy Test of the Ni | Na-X | NiO₂ Battery.

The measurements were obtained in the frequency range from 100 Hz to 1 MHz with the help of a Hewlett Packard impedance analyzer applying a constant bias voltage of 0 V and a modulating voltage of 500 mV. Then, the real (Z_r) and imaginary (Z_i) parts of the complex impedance were calculated from the measured impedance. These measurements were also applied to the study of the produced silica aerogels.

Task 6. Students Participation.

Two (2) graduate and two (2) undergraduate students have been taking part in the synthesis and characterization of the produced materials, the construction of the equipment and other tasks. These students have received a very good training in the sol-gel methodology for solids synthesis, the characterization of materials with TG, XRD, FTIR, adsorption and dielectric methods.

Task 7. Seminars and Students Participation.

Group seminars were delivered every Friday at 3.00 PM. During the year 37 seminars were delivered in which the members of the research group were informed about the theory and practice relating to the topics of the proposal in particular and with the field of Materials Science in general.

Task 8. Travel.

On November 21, 2008, Dr. Roque-Malherbe attended a meeting at the Center of Integrated Nanotechnologies (CINT) in Albuquerque New Mexico. During this meeting, which was organized by the Massie Chair Program Officer Ms. Malika Hobbs, Dr. Robert Q. Hwang Co-Director of CINT delivered a presentation explaining the aims of this institute and the possibilities of collaboration between CINT and the different organizations belonging to the Massie Chair program. The meeting also provided the opportunity for, Dr. Roque-Malherbe to become acquainted with Dr. Mohamed F. Chouikha, from Howard University, Dr. Joshua T. Moore from Tennessee State University, Dr. Okenwa O.I. Okoli from Florida State University and Dr. Nosa O. Egiebor from Tuskegee University.

In June 23-26, 2009 Dr. Roque-Malherbe, attended the International Conference Diffusion in Solids and Liquids 2009, held in Rome, Italy.

From June 29 to July 1 2009, Dr. Roque-Malherbe, made a short stay at the Institute of Materials Science at the University of Valencia, Spain, in order to carry out arrangements to continue the collaboration between the universities.

IV. Accomplished Tasks 2009-2010

Task 1. Silica Characterization Methods. Scanning Electron Microscopy.

The scanning electron microscopy (SEM) study was performed, with a JEOL CF 35 scanning electron microscope in secondary electron mode at an accelerating voltage of 25 kV to image the surface of the studied samples. These samples were attached to the sample-holder with an adhesive tape and then coated under vacuum by cathode sputtering with a 30–40 nm gold film prior to observation. The

surface morphology was revealed from SEM images and the average grain size was estimated, albeit qualitatively.

Carbon Dioxide Adsorption.

In order to study carbon dioxide adsorptions were obtained, in an upgraded Quantachrome Autosorb-1 automatic physisorption analyzer, the adsorption isotherms of CO_2 at 273 K in samples degassed at 573 K during three hours in high vacuum (10^{-6} Torr). In this case, as the carbon dioxide vapor pressure, P_0 , at 273 K, was high, that is: $P_0 = 26,141$ Torr; we worked in the following relative pressure range: $0.00003 < P/P_0 < 0.03$. Experience indicates that the adsorption process in this range is very well described by the Dubinin adsorption isotherm equation in the case of carbonaceous materials and other adsorbents. The Dubinin-Astakhov (D-A) adsorption isotherm equation can be represented in a log-log scale as follows [1-3]:

$$\ln(n_a) = \ln(N_a) - \left(\frac{RT}{E}\right)^n \ln\left(\frac{P_0}{P}\right)^n \quad (1)$$

This relation, describes the relation between the amount adsorbed, n_a , and the inverse of the relative pressure, i.e., P_0/P . Where, E , is a parameter named the characteristic energy of adsorption, N_a , is the maximum amount adsorbed in the volume of the micropore, and, $n(1 < n < 5)$ is an empirical parameter. This equation is a very powerful tool for the description of the experimental data of adsorption in microporous material [4-6]. The fitting process of equation "1" allows us to calculate the best fitting parameters, i.e., N_a , E , and n . If, n , is considered a constant, for example, $n = 2$, we will get the Dubinin-Radushkevitch (D-R) equation that will be the concrete equation applied here. Then, with the help of the CO_2 adsorption isotherms and equation "1" with: $n = 2$, the micropore volume, $W_{MP} = N_a V_L$, (where V_L is the molar volume CO_2 at 273 K) and the characteristic energy of adsorption, E , [kJ/mol] were measured.

Thermogravimetric Analysis.

The TGA testing process was carried out with a TA, Q-500 equipment [3]. To make the TGA test, the samples were placed into a ceramic sample holder, which was suspended from an analytical balance. Then, the sample holder was heated according to a predetermined thermal cycle, that is: the temperature was linearly scanned, from 23 to 800 °C, at a heating rate of 5 °C /min, in a flow of 100 ml/min of the purge gas that is pure N_2 . The data collection, the temperature control, the programmed heating rate, and the gas flow control, were automatically controlled by the software of the TA, TQ500 TGA. The TGA data was collected as a *Wt. %* versus T (°C) profile, where: $Wt.\% = (M_t/M_0) \times 100$, is the per-cent ratio of the sample mass during the thermal treatment, M_t , and the initial mass of the sample M_0 .

Small Angle X-ray Scattering.

The small angle x-ray scattering (SAXS) [7-13] experiment, was carried out with a Bruker D8 Advance system in transmission configuration. The SAXS data is normally plotted as: $I(q)$ (intensity) versus $q = (4\pi/\lambda)\sin(\theta)$ ($\lambda = 0.1542$ nm) on log-log scale. In these plots are normally observed the Porod power law region [8-10]:

$$\ln[I(q)] = \ln B - 4 \ln[q] \quad (2)$$

In which: B is a constant, and the Guinier power law region [10]:

$$I(q) = G \exp\left[-\frac{R_g}{3} q^2\right] \quad (3)$$

Where: G is a constant and R_g is the radius of gyration. The SAXS data was only applied here to calculate the primary particle diameter, $\phi_{V/S}$, using the Porod data, as follows [11]:

$$\phi_{V/S} = \frac{6Q}{\pi B} \quad (4)$$

Where:

$$Q = \int_0^{\infty} q^2 I(q) dq \quad (5)$$

Is the Porod invariant.

Diffuse Reflectance Infrared Fourier Transform Spectrometry.

A Thermo Scientific Nicolet iS10 FTIR spectrometer with the Smart Collector for diffuse reflectance analysis and the environmental chamber for the smart collector was applied to achieve the diffuse reflectance infrared Fourier transform spectra. The spectra were collected with a resolution of 4 cm^{-1} and were made 100 scans per sample [14].

A background with KBr (FTIR pure, provided by Nicolet) located in the sample holder of the environmental chamber was made applying the same conditions to get the sample spectrum in the case of the dehydrated samples an later used to achieve the sample spectra. In order to dehydrate the samples, they were heated, at $300 \text{ }^\circ\text{C}$, under N_2 (Praxair, 99.99 %) flow at a rate of 50 cc/min during 2 hours. Lastly, the spectra of the dehydrated silica were obtained with the sample inside the environmental chamber, at room temperature, under N_2 (Praxair, 99.99 %) flow at a rate of 50 cc/min [14].

The background taken was the sample dehydrated at $300 \text{ }^\circ\text{C}$. to get the IR spectra of carbon dioxide adsorbed on the silica surfaces. Thereafter, a flow of CO_2 (Praxair, 99.99 %) was passed at a rate of 50 cc/min during 3 minutes. Then, the samples were purged under N_2 (Praxair, 99.99 %) flow at a rate of approximately 50 cc/min during one minute; and for some samples for seven minutes to desorb the weakly bonded carbon dioxide. Finally, the spectra were obtained with the sample inside the environmental chamber to get the spectra of the carbon dioxide molecule adsorbed on the silica surface [14].

Task 2. Study of the Silica Morphology

All the silica sphere packing (SP) and particle packing (PP) materials and the aerogels AER were morphologically characterized with the help of nitrogen adsorption and SEM [14]. The morphological characterization was made with the help of nitrogen adsorption at 77 K in order to measure S^{BET} , W^{mic} , W and d^{mic} and d^{mes} . The results obtained are reported in Table 1. It is evident from the reported data that both aerogel samples also showed a complex pore structure with a considerable micropore region and a very developed mesopore region. Below, are more details about the morphology of all these silica.

Table 1. Morphological data of the particle packing materials and both aerogels [14-16].

Sample	S^{BET} [$m^2 g^{-1}$]	W^{Mic} [$cm^3 g^{-1}$]	W^{DFI} [$cm^3 g^{-1}$]	d^{Mic} [nm]	d^{Mes} [nm]
PP-70bs2	1600 ± 500	0.18 ± 0.05	3.0 ± 0.5	0.55	6.5
PP-74bs5	1200 ± 400	0.14 ± 0.05	1.7 ± 0.5	0.57	6.1
PP-68bs1e	1500 ± 500	0.27 ± 0.05	2.4 ± 0.5	0.55	8.1
PP-75bs1	1400 ± 500	0.16 ± 0.05	2.7 ± 0.5	0.57	12.5
AER-309	500 ± 100	0.16 ± 0.05	4.2 ± 1.0	0.58	50.0
AER-909	1000 ± 200	0.4 ± 0.1	2.0 ± 1.0	0.57	7.3

Note: PP means particle packing silica xerogels and AER are silica aerogels

In Fig.1, the SEM images of the sphere packing silica SP-80 and SP-FM3a-GEO are reported. In these micrographies the spherical form of the Stöeber silica are evidently shown. The diameters of these spheres, ϕ^{SEM} [nm], are reported in Table 3. Also, in Fig. 1 a micrograph of the particle packing silica PP-68bs1e is shown. In this micrography it is obviously revealed that the spherical geometry was broken, due to the use of an amine instead of ammonium hydroxide as catalyst⁶⁹. The diameter of the particles PP-68bs1e is: $\phi = 1 - 5 \mu m$.

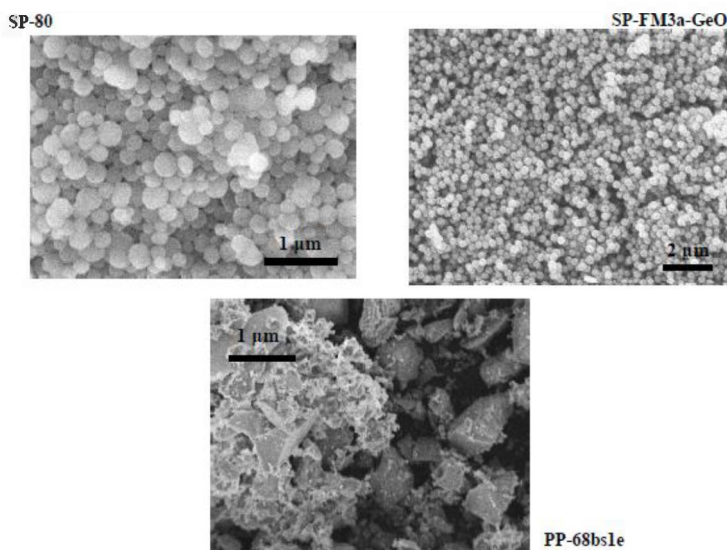


Fig. 1.

The pore size distribution (PSD), in the micropore range, calculated with the help of the Saito-Foley method, specifically for: SP-69b, PP-68bs1e, MS-ZSM-5-5020 and MS-DAY, which are typical SP, PP and MS are shown in Fig. 2. In Table 3 and 4 are reported the SF-PSD pore width mode d^{Mic} [nm] [3].

Small-angle x-ray scattering (SAXS) is one of the main tools applied to investigate the morphology of particle aggregates, since it allows to probe structure over several orders in length scale in the nano region, including both primary particles and aggregates⁸³⁻⁸⁸. In Fig. 3 are shown the SAXS data corresponding to the PP-68bs1e. The results obtained for these parameters are reported in Table 6. It is now necessary to state that we did not studied by SAXS the SP samples, as they are very well studied with this method [7-13].

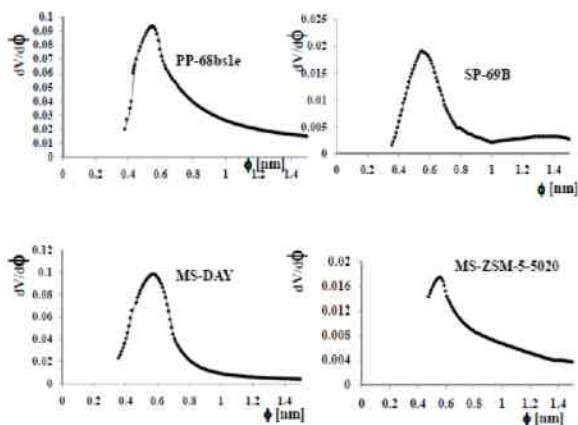


Fig. 2

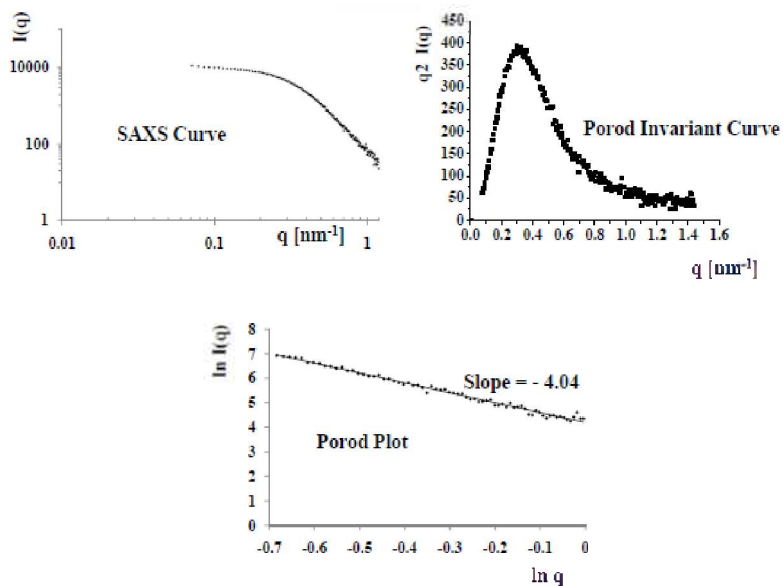


Fig. 3

The previously reported morphologic data of the SP and PP silica samples indicate that these adsorbents have a complex pore structure including micropores and mesopores. This morphology is a result of the particular internal morphology of the SP and PP silica which are composed of the secondary particles evidenced by SEM where these agglomerates are composed of primary particles. That is, the observed morphology is explained by the agglomeration of the primary particles, revealed with the help of the SAXS study, to form the secondary particles, since in the agglomeration process are created voids spaces between the composing primary particles. This morphology will be reflected in the adsorption of carbon dioxide as will be later explained.

The TGA reported here were taken under N_2 flow from 25 to 800 °C. The thermal gravimetric profiles of the SP silicas are shown in Fig. 4; those of the PP silicas in Fig. 5 and Fig. 6.

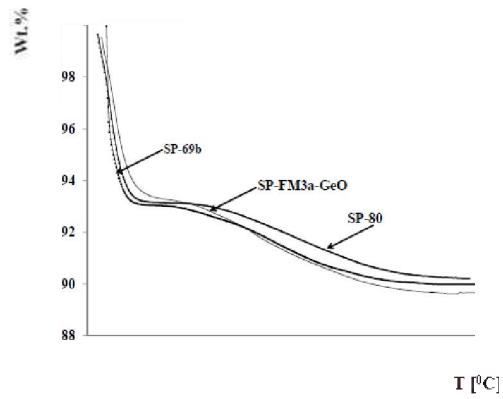


Fig. 4

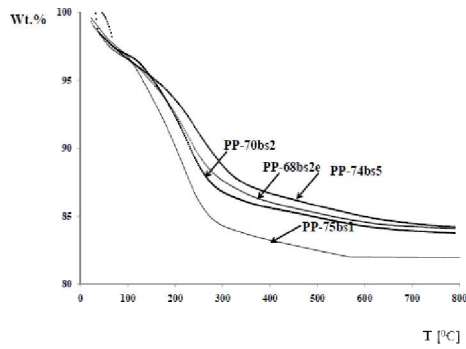


Fig. 5.

At relatively low temperatures, that is below 200 °C, the release of loosely linked water takes place. The differential TGA peaks of dehydration and dehydroxylation were applied to determine the position of this point. It was set at: 200 °C (see Fig. 6); at temperatures higher than 200 °C the surface silanol groups begins its condensation to form water molecules [14]. Finally, at 700-800 °C only isolated silanols are present in the surface [14].

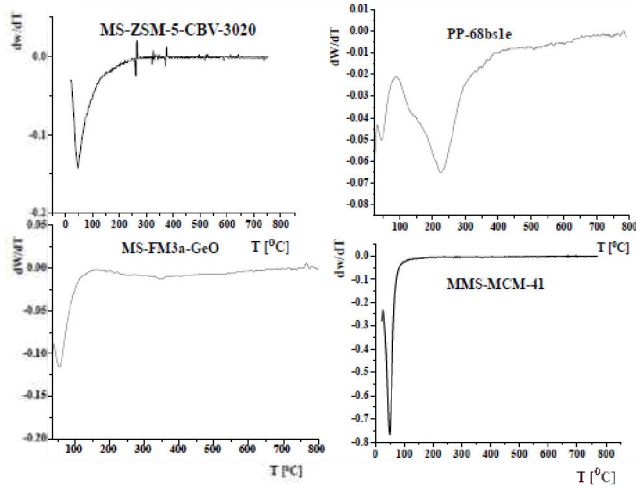


Fig. 6.

We have previously measured the specific surface area of the produced amorphous silica with the help of the BET method [15,16]. This method shows normally a 20 % relative dispersion of the results. However, for samples with a very high specific surface area the relative error is bigger [1-3], about: 30 %. In this regard we have applied an innovative methodology to confirm the BET data applying the TGA profiles of the amorphous silica xerogels

In order to calculate the silica specific surface area with the TGA data, a very well-known fact [17] explicitly, that in a fully hydroxylated silica the specific amount of OH , i.e., $\sigma \approx 4.5 OH/nm^2$, can be considered a constant (the Kiseliiov-Zhuralev constant), independent of the silica type [14]. In this regard, the specific amount of OH can be calculated with the help of the TGA profile, as follows [17]:

$$\sigma = 2 \left(\frac{\Delta W_{H_2O}^T}{M_{H_2O} N_A S} \right) \quad (6)$$

Where: $\Delta W_{H_2O}^T = Wt.\%(200^\circ C) - Wt.\%(700^\circ C)$, in which: $Wt.\% = (M_T/M_0) \times 100$, is the per-cent ratio of the sample mass during the thermal treatment, M_T , is the mass of the sample at temperature, T , and, M_0 , is the initial mass of the sample. The factor 2 implies that each water molecules requires two OH groups to be formed; M_{H_2O} , is the molecular weight of water; N_A , is the Avogadro number and; S , is the specific surface are of the silica.

The use of the TGA method for this purpose has a weak point, i.e. the determination of the end of the process of physically adsorbed water release; that is, the separation of the dehydration and dehydroxylation processes. In the present study, as was previously commented, we applied the differential TGA peaks of dehydration and dehydroxylation (see Fig. 6) in order to determine this point. Then, if we consider that $\sigma = 4.5 OH/nm^2$ as a constant, then, with the expression [14]:

$$S^{TG} = 2 \left(\frac{\Delta W_{H_2O}^T}{M_{H_2O} N_A \sigma} \right) \quad (7)$$

We can calculate the specific surface area, with the help of the TGA method. In Table 2 are reported the obtained values. These results coincide within the error magnitude with the S^{BET} values reported in [16,17].

However, these results do not exhibit a big dispersion, as was the case for the values reported in Table 4; that is, the relative error was 15-20 %. Then, with a novel methodology, specifically developed for the calculation of the specific surface area of silica, was confirmed the extremely high specific of the PP silica and were obtained more precise and accurate values.

Table 2. Specific Surface Area Calculation Applying the TGA Data.

Note: SP means sphere packing silica xerogels and PP means particle packing silica xerogels.

The results reported above allows us to state that the studied amorphous silica sphere packing and particle packing has a particular internal morphology which is composed of the secondary particles evidenced by SEM (see Fig. 1); that is, aggregates, whose diameters, are around 300 nm for the SP and 1000 nm for the PP (see Fig. 1). These agglomerates are composed of primary particles of around 15-20 nm [14] for the SP silica and 7 nm for the PP silica. The observed microporosity is explained by the agglomeration of the primary particles to form the secondary particles, since in the agglomeration process voids spaces are created between the composing primary particles. To be exact, the SP, PP and AER samples shows micropores with: $d^{Mfc} = 0.56 - 0.59 \text{ nm}$ [14] and mesopores with $d^{Mes} = 4 - 8 \text{ nm}$ for the SP $d^{Mes} = 6 - 12 \text{ nm}$ for the PP and bigger for the aerogels, that is $d^{Mes} = 7 - 50 \text{ nm}$. The specific surface area of the PP and one of the AER silicas are 2-3 times bigger than those of the SP silicas and also 1.5 bigger that those of the MMS-MCM-41. These facts, made the PP silica and one of the AER-909 samples very good materials for large specific surface area applications as adsorbents and catalyst supports.

Task 3. Silica Surface Chemistry.

To complete the characterization of the tested silica, we needed to study its surface chemistry. For the study of this topic, the silica samples were carefully dehydrated in the environmental chamber for the smart collector of the Nicolet iS10 FTIR spectrometer as was previously explained. In Fig. 7 are shown the DRIFT spectra of the dehydrated sphere packing silica in the range between: 4000-2700 cm^{-1} . In Fig. 8 are shown the DRIFT spectra of the dehydrated particle packing silica in the range between: 4000-2700 cm^{-1} and finally in Fig. 10 are shown the DRIFT spectra of the dehydrated AER-309 and the MMS-MCM-41, the MS-SSZ-24 and the MS-ZSM-5-5020, also in the range between: 4000-2700 cm^{-1} .

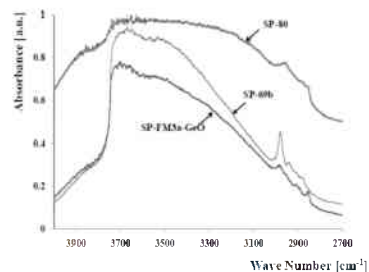


Fig. 7

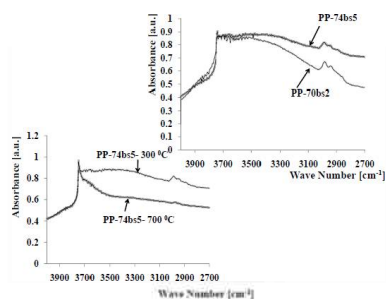


Fig. 8.

In relation to the bands present in the recorded DRIFTS spectra, the most important are those related to the hydroxyl functionalities, that is: vicinal, geminal and isolated silanol sites [2,3,14]. Explicitly, the $O-H$ fundamental stretching vibration range, i.e. $3800-3000\text{ cm}^{-1}$; where, the terminal free OH group, which is not H-bonded, show a narrow absorption band at about: $3720-3730\text{ cm}^{-1}$; while the vicinal and germinal OH groups, which are H-bonded, show a broad absorption band, which results from the superposition of different hydrogen bonded interacting OH groups [14]. These bands are present in all the obtained spectra (see Figs. 7 and 8). Specifically, the pattern of bands shown by these spectra is in a general sense similar for all the studied samples. Consequently, the studied samples have a surface chemistry typical of silica, showing: free silanol groups and vicinal and geminal silanol groups. Additionally, in the DRIFTS spectrum of the sample PP-74bs5 (Fig. 8) after heating it at $700\text{ }^{\circ}\text{C}$, is evident an increase in the intensity of the free OH group and a decrease of the band corresponding to vicinal and germinal OH groups. This fact corresponds to the effect of heating a silica, whose outcome is the production of a siloxane site, one water molecule, and an isolated SiOH group [14].

Task 4. Measurement of the Micropore Volume with Carbon Dioxide Adsorption

In Fig. 9 are reported the Dubinin plots of the adsorption isotherms of carbon dioxide at 273 K on the silicas: SP-80, SP-69B, FM3a-GeO, PP-68bs1e and PP-75bs1

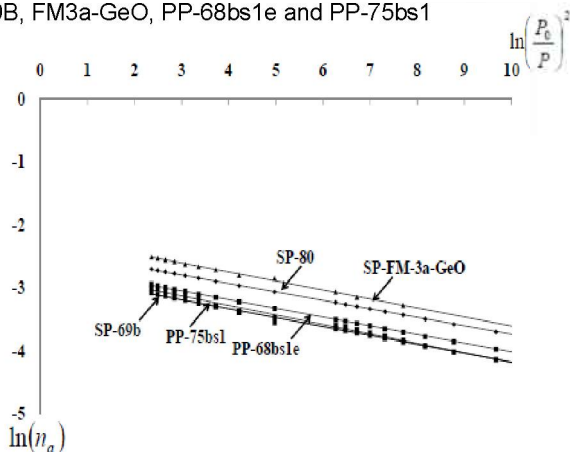


Fig. 9.

The values of the micropore volume measured with the help of carbon dioxide adsorption, $W_{MP}^{CO_2}$, are reported in Table 3. This parameter was measured by fitting equation "1", with: $n = 2$, to the data reported in Figs. 9. The reported results indicate, as was previously shown with the help of nitrogen adsorption at 77 K, that the samples exhibit a developed micropore region, in addition to the mesopore portion of the silica framework. It is necessary to state then that carbon dioxide adsorption takes place only in the micropore region. This is evident because of the excellent fitting of the obtained data by the D-R isotherm.

The developed micropore adsorption space measured with carbon dioxide adsorption is in agreement with the nitrogen adsorption morphological data discussed in the previous section.

Table 3. Parameters Calculated with the Dubinin-Radushkevish Equation

Sample	R^2	E^{CO_2} [kJ/mol]	$q_{iso}^{CO_2}(0.37)$ [kJ/mol]	$W_{MP}^{CO_2}$ [cm ³ /g]
SP-69	0.9997	24	28	0.21
SP-80	0.9999	24	28	0.13
SP-FM3a-GeO	0.9998	24	28	0.23
PP-68bs1e	0.9998	24	28	0.17
PP-75bs1	0.9998	23	27	0.23

Task 5. Student Participation.

Two (2) graduate and two (2) undergraduate students have been taking part in the synthesis and characterization of the produced materials, the construction of the equipment and other tasks. These students has received a very good training in the sol-gel methodology for solids synthesis, the characterization of materials with TG, XRD, SAXS DRITS, SEM and adsorption methods.

Task 6. Seminars and Students Participation.

Group seminars has been delivered every Friday at 3.00 PM, During the year 31 seminars In these seminars were delivered the members of the group have been informed about the theory and practice related of the topics of the project and with the field of Materials Science in general.

Task 7. Travel.

From June 23 to June 26 2010 Dr. Roque-Malherbe, attended the International Conference Nanotech, 2010 held in Anaheim, California

From June 27 to June 29 2009, Dr. Roque-Malherbe, made a short stay at the Department of Mechanical and Materials Science Engineering at Florida International University, in Miami, Florida, in order to deliver a talk entitled Physical Chemistry of Materials a New Field in Materials Science.

V. Conclusions

As was evidenced, above, the initial goals of the project, namely, the synthesis and characterization of low refractive index aerogel silica for Cherenkov counters was changed to the synthesis and characterization of extremely high specific surface area aerogel silica for gas storage. The change was made based on the cost necessary to produce the low refractive index aerogel silica, as it would have been necessary to make several supercritical drying process where the amount of liquid carbon dioxide was very high and that is our budget did not allow us to afford this task. However, silica aerogels prepared by the Sol-Gel processing method and dried by supercritical drying are excellent adsorbents.

Currently, the process of gas capture and storage by gas adsorption in solid adsorbents is one of the most important tasks of Materials Science. For example, with this methodology the carbon dioxide levels in the atmosphere can be reduced. Additionally, the recovered carbon dioxide can be reused for industrial applications.

The elevated cost of carbon recovering or capturing, at present, prevent the economical separation of carbon dioxide from gases. The main costs associated with this process are in the carbon dioxide separation step. Normally, this procedure is carried out by gas-liquid absorption-stripping processes applying aqueous solutions of alkanolamines, where the gas absorption process is particularly energy-intensive for renewal of the solvents and is as well overwhelmed by corrosion problems. Adsorption is well established as a unit operation for the production of pure gases and for the treatment of waste streams. Gas mixtures can be separated with adsorbents applying three physical processes: equilibrium, kinetic partitioning and molecular sieving. In this regard, adsorption technologies are applied for diverse gas-separation processes specifically for the separation of carbon dioxide. Even though the majority of adsorbent materials, such as: carbonaceous adsorbents, molecular sieves, alumina or silica gel can be applied for carbon dioxide separation, applying the pressure swing adsorption (PSA) process, activated alumina is currently considered the most suitable sorbent for removing water and carbon dioxide from air in a PSA process. However, modified silica materials with high specific surface area are currently widely studied as carbon dioxide adsorbents. Particularly, the impregnation of amines in mesoporous silica is a flourishing field of research. Nevertheless, these amines are not stable at high temperature given that these organic substances, on the surface, begin to decompose at about 200 °C, then restraining the application of these materials as adsorbents which require high-temperature regeneration. Consequently, another form of modification of silica is by loading alkali metals and other metal in the silica surface; since carbon dioxide, being amphoteric in nature, will strongly interact with the formed Lewis acid centers.

Consequently, notwithstanding the fact that the subproject was modified we obtained extremely high specific surface area silica aerogels very promising for applications in gas separation and storage. The Cherenkov counters radiation detectors are the method for the sensing elementary particles that are normal issues in nuclear physics. However the development of the transparent silica gel was very expensive. We developed a high specific surface area silica gel that have applications in gas drying, cleaning operation useful in nuclear industry in process. This fact justifies the necessary change. This fact justifies the necessary change.

Sub-Project 2: Investigation Study of Magnetic and Electronic Transport Properties at Material Interfaces in Magnetic Multilayer Heterostructure using Gd. – Dr. Yazan Hijazi

As a result of the Massie Chair research activities under sub-project 2 from 2006 to 2011, the UT Massie Chair team developed the capability and infrastructure to produce high quality thin-film magnetic films and magnetic multilayer structures with fine control over film quality and thickness using sputter deposition capability to perform in-house electric and magnetic characterization of these films. Furthermore, the team has been able to experimentally quantify the effect of Gd incorporation within the magnetic multilayer structure and produce magnetic media with exchanged decoupled multilevel magnetic anisotropy. The stated objectives of this research sub-project have been satisfied fully, with the exception of a minor and necessary strategy change in year 3 which required the team to shift funds marked for the purchase of an Atomic Force Microscope to the building of an in-house Kerr microscope for magnetic characterization. This strategic change had no effect on the required measurements and characterizations as these characterizations were fully completed at the facilities of our collaborators at Florida International University and the University of Puerto Rico. The details of this strategic change are fully explained below under the Infrastructure Development section.

The project milestones can be summarized as follows: 1) Attainment of stable and reliable processes that produce the corresponding thin films with excellent properties and production of Co/Pd and Co/Pt multilayer's with strong perpendicular magnetic anisotropy and repeatability, 2) Successful stacking of magnetically independent Co/Pt multilayer's and determination of optimal parameters for the exchange decoupling layer, 3) Determination of minimum pattern size at which magnetic domains become single domain, and 4) Completion of a in-house magnetic hysteresis loop characterization system.

This report provides a quick summary of stated objectives and degree of accomplishment of each, followed by a more detailed illustration of the objectives and their results.

Year 1 Objectives: Completed fully

1. Acquired three-target RF/DC magnetron sputtering system for sample deposition.
2. Procured required target materials, process gases and installed required infrastructure.
3. Installed sputtering system and verified proper operation.

Year 2 Objectives: Completed fully

1. Began sample deposition, characterize films in terms of surface morphology and crystallographic orientation, and established sputter rates and deposition parameters for all target materials.
2. Acquired Kerrmicroscopy (MOKE) system for magnetic hysteresis characterization. (**System was built in-house, completed and validated in 2011**)
3. Hired 2 undergraduate students and train them to perform sample preparation and characterization tasks. This will include proficiency of RF/DC sputtering and incremental training in sample characterization as the project unfolds.
4. Produced samples and send for further characterization through existing collaborations with the University of California Riverside, and Florida International University. Measurements such as Ferromagnetic Resonance (FMR) and cryogenic temperature electronic transport were performed.

Year 3 Objectives: Completed fully with exception of Objective # 1 (Explained Below)

1. Acquired Atomic Force Microscopy (AFM) System capable of Magnetic Force Microscopy (MFM) and Scanning Tunneling Microscopy (STM). **The AFM was not purchased as explained below:**

This objective addresses the ability to perform surface characterization on the deposited films and this system was not purchased. This stemmed from the fact that the price of a readymade Kerr-Microscopy system turned out to be significantly higher than initial estimates requiring the team to develop the system in-house. Furthermore, since the project's main focus is magnetic multilayer development the availability of a magnetic characterization tool far outweighs the need to perform surface characterizations. Therefore, a decision was made to build the Kerr-Microscope in-house using the funds marked for the Atomic Force Microscope, while all the required Atomic Force Microscopy measurements were completed at collaborator institutions (*Florida International University and University of Puerto Rico*).

2. Acquired vibration isolation table to perform vibration sensitive measurements.
3. Depending on initial data of magnetic and electronic measurements, produced variations of heterostructures configurations with Gd and/or Nd for further investigation of the effect of said materials on the magnetic and electronic properties.
4. Continued collaborative work in order to better quantify and understand the role of f-electrons in observed and measured phenomena.

Year 4 Objectives: Completed fully

1. Acquired electromagnet system capable of 7 Tesla magnetic field biasing, which will serve as base for building future Ferromagnetic Resonance (FMR) system in order to perform spin-based measurements in-house.
2. Quantified the effect and potential uses of using Gd in magnetic multilayered structures, and identify areas of future research work.
3. Reported and published results.

To elaborate on the results of sub-project II, the detailed project objectives are mapped to activities and deliverables in three functional areas: 1) Student Development. 2) Infrastructure Development. 3) Research Development.

Task 1: Student Development

The following objective was stated:

1. Hire undergraduate engineering students and train them to perform sample preparation and characterization tasks. This will include proficiency of RF/DC sputtering and incremental training in sample characterization as the project unfolds.

This objective has been completely satisfied; in fact the impact of student development and outreach activities greatly surpass the stated objective. A total of 10 undergraduate students have directly worked and benefitted from this project, four (4) of whom actively participated in the research effort without funding support for at least one semester. The students acquired soft research skills pertaining to the scientific method and hypothesis testing, data analysis, and literature review, among others. Moreover, they attained practical knowledge through regular research seminars in the following: 1) Magnetic Phenomena: Fundamentals, Measurement, Characterization, Magnetic Multilayer Applications, Nano-magnetics. 2) Thin-film Deposition: CVD and PVD techniques. 3) Thin-Film Fabrication and Characterization techniques. 4) Nuclear Radiation: Fundamentals, Measurement and Sensing. These seminars were advertised and open to all engineering students; therefore, the total number of engineering students that benefitted from these activities is estimated between 50 to 70 students. The activities included:

- Weekly informal research progress reports.
- Biweekly meetings identifying completed tasks, obstacles, and drafting task list in support of research objectives.
- Biweekly research seminars.
- Deposition of magnetic and non-magnetic thin-films and structures using RF and DC magnetron sputtering.
- Characterization of thin-film surface roughness and thickness using AFM.
- Perform periodic equipment maintenance.
- Commission and validate newly acquired equipment.
- (15) Visits to the University of Puerto Rico in Cayey, where students learnt about SEM and were trained to use AFM to determine film thickness and surface roughness.
- Tutorial sessions on Lab-View for experimentation and instrument control.
- Participation and presentation of work in the yearly UT-organized *Researcher's Meeting*.
- Reading and analysis of publications relevant to research work.
- Informational sessions showcasing the project and facilities to K-12 students organized through the yearly UT open day events.

Task 2: Infrastructure Development

The research objectives set forth required substantial infrastructure to accomplish. The required tools and techniques were practically inexistent at the UT School of Engineering. Accordingly, significant effort was spent in working with key collaborators, and developing a capable in-house infrastructure to: 1) ensure delivery on research objectives, 2) ensure post-grant research continuity and 3) have available equipment, tools and know-how in support of future research and funding in relevant areas. The activities undertaken support: 1) securing and setting up lab space including installing special power outlets, gas and water cooling lines, and 2) acquiring necessary equipment, tools and supplies to perform sample preparation and characterization.

The following objectives were stated:

1. Acquire three-target RF/DC magnetron sputtering system for sample deposition.
2. Procure required target materials, process gases and install required infrastructure.
3. Install sputtering system and verify proper operation.
4. Acquire vibration isolation table to perform vibration sensitive measurements.
5. Acquire electromagnet system capable of 2 Tesla magnetic field biasing.

The stated objectives have been satisfied. A four-target sputtering system (*ATC-4 Orion Series*) has been acquired from *AJA International*. This system is the heart of the operation. The recipes of structures to be fabricated are entered into recipe files that automatically control the deposition parameters of pressure, power and deposition time. This allows highly complex and repeatable structures to be fabricated with minimal effort and with fine control over film quality. The system is equipped with two DC and one RF power supplies, three vacuum gauges, rotating sample holder with a heater up to 500°C, and state of the art Labview control. Moreover, it was acquired with expansion in mind; these easy upgrades include: thickness monitor, load-lock, and reactive sputtering capability. The system proved user-friendly and reliable. However, several component failures resulted in ninety percent uptime. Nonetheless, these issues were promptly handled by *AJA* under warranty.

As the project unfolded a strategic decision was made that affected the proposed course of action. This was adequately reported in the quarterly reports, and did not affect the overall mission of the project. This relates to the following objectives as is explained below:

6. Acquire Kerrmicroscopy (MOKE) system for magnetic hysteresis characterization.
7. Acquire Atomic Force Microscopy (AFM) System capable of Magnetic Force Microscopy (MFM) and Scanning Tunneling Microscopy (STM).

Objectives six and seven address magnetic and surface characterization capabilities; respectively. In particular, the *Kerr-microscopy* capability is a high value objective that probes the magnetic properties of the deposited structures. In preparing the proposal the Co-PI made initial price projections based on informal conversations with colleagues knowledgeable in such systems. However, quotations from four vendors revealed that such a system will cost anywhere from \$60,000 to \$140,000. This was well out of budget bounds; therefore, a strategic decision was made: to perform AFM-related

measurements at collaborators facilities and use the liberated funds to build a homemade *Kerr-microscopy* system. This decision required a shift in focus and significant time and effort to develop and build the system. Nonetheless, this has had great benefits with respect to student experience and skills acquired, institutional knowledge gained, and competency development.

Figures 1 and 2 show the sputtering system, power supply and gauss meter used in the Kerr-microscope system.



Fig. 3.1 Sputtering System



Fig. 3.2 Bipolar supply and Gauss meter

Task 3: Research Development

Research activities spanned the following sequence: 1) initial deposition and surface characterization of films, 2) developing hetero-structures and recipes that incorporate magnetic and non-magnetic films in unique ways, 3) magnetic characterization and identifying interesting structures, 4) incorporating Gd within these structures followed by magnetic characterization, identification of interesting structures and optimization of the process. Over 250 samples were deposited and a total of 5 individual studies carried out.

The following objectives were stated and completely satisfied.

1. Begin sample deposition, characterize films in terms of surface morphology and crystallographic orientation, and establish sputter rates and deposition parameters for all target materials.

Milestone: A stable and reliable process has been achieved to produce films of Ta, Co, Pd, Gd, Pt, and Ti with rms surface roughness range of 0.16 to 0.25 nm, with good thickness control.

Over 50 samples were characterized during the course of two trips to the Motorola Nanofabrication labs at Florida International University in Miami. Measurements were done to 1) determine the sputter rate, and 2) improve the surface morphology. The measurements include *rms* surface roughness using *Atomic Force Microscopy (AFM)*, thickness measurements using profilometry, crystallography using *X-ray diffraction*, and surface magnetization using *Magnetic Force Microscopy*. This was an iterative process by which the film quality has been successively improved through incremental improvements in the recipes. **The result is the ability to produce high-quality thin-films that are smooth with nanometer control on thickness of the following materials: Cobalt, Tantalum, Palladium, Platinum, Titanium and Gadolinium.** Figure 3 through 5 show AFM/MFM data for Cobalt, X-ray diffraction data for Palladium, and fitted sputter rate for Tantalum.

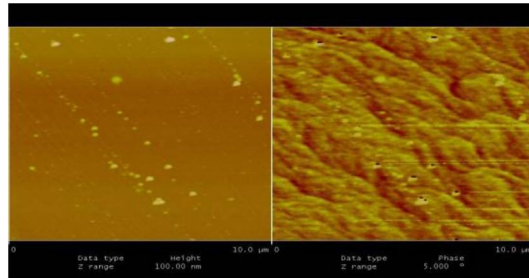


Fig. 3.3 AFM (left) and MFM (right) of typical Cobalt film as deposited. MFM shows striated magnetic domains

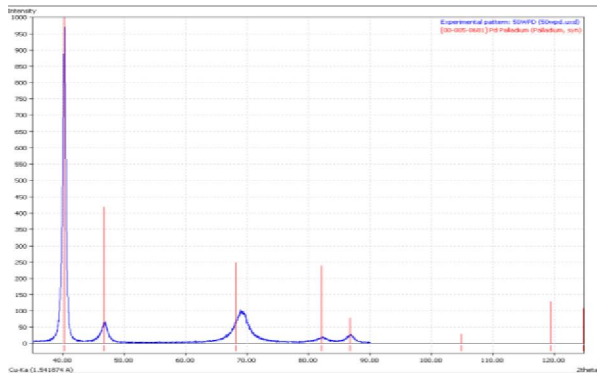


Fig. 3.4 X-Ray diffraction data for Palladium shows (111) dominant orientation

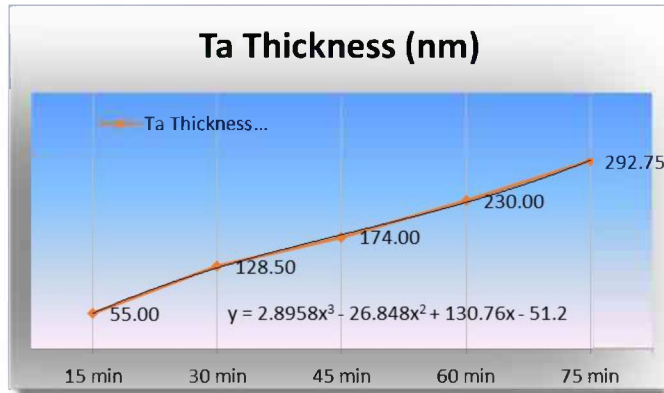


Fig. 3.5 Experimental and fitted Tantalum sputter rate

2. Produce hetero-structure samples and send for further magnetic characterization through existing collaborations with the University of California, Riverside; and Florida International University.

Milestone: Produce multilayers of Co/Pd and Co/Pt with strong perpendicular magnetic anisotropy.

Milestone: Patterning of Co/Pd multilayer's using FIB produces single magnetic domains

The perpendicular magnetic anisotropy in the *Co/Pd* and *Co/Pt* systems studied is a result of the interface exchange coupling between the magnetic and non-magnetic layers, and not due to the crystalline structure. This requires very smooth films and matching materials to have excellent interface quality between the individual layers. This has been achieved through careful process improvement and control over deposition parameters. Media with the following structures have been produced that show good perpendicular magnetic anisotropy:

- a. $\text{Ta}_{50\text{nm}}/\text{Pd}_{3\text{nm}}/[\text{Co}_{1\text{nm}}/\text{Pd}_{0.2\text{nm}}]_{15}/\text{Pd}_{5\text{nm}}$
- b. $\text{Ti}_{4\text{nm}}/\text{Pt}_{0.55\text{nm}}/[\text{Co}_{0.3\text{nm}}/\text{Pt}_{0.55\text{nm}}]_{10}/\text{Pt}_{5\text{nm}}$

The patterning of Co/Pd media was carried out as part of study at FIU using *Focused Ion Beam* (FIB) in order to determine the maximum pattern size at which the media becomes single domain. Figure 6 shows single magnetic domains at a pattern size of 110nm. This is particularly interesting for nano-patterned sensor arrays.

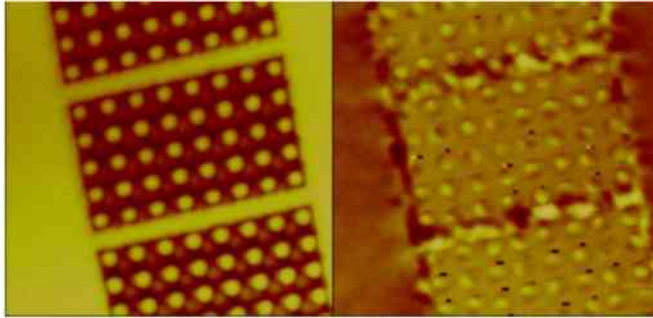


Fig. 3.6 AFM (left) and MFM (right) of 110nm patterned Co/Pd with single perpendicular domains

3. Depending on initial data of magnetic and electronic measurements, produce variations of heterostructures configurations with Gd and/or Nd for further investigation of the effect of said materials on the magnetic and electronic properties.

Milestone: Optimized seed layer of Ti/Pt for Co/Pt system with improved coercivity.

Milestone: Incorporating Gd within the multilayer structure of Co/Pt system showed progressive deterioration of coercivity over the thickness range from 0nm to 0.6nm.

The seed layer system Ti/Pt has been evaluated with a bi-layer structure of $(\text{Co}_{-1\text{nm}}/\text{Pt}_{0.2\text{nm}})_{x15}$; the structures were evaluated per their magnetic anisotropy and coercivity. Samples with no seed layer served as a benchmark and displayed randomized in plane and out-of-plane anisotropy. While the thickness of the Ti was varied from 0.5nm to 5 nm, and the second layer of Pt was varied through several nanometers. It was found that the thickness of the Ti/Pt seedlayer may be brought down to 4.5nm with 0.5nm Pt with improved coercivity and squareness of the hysteresis loop. Figure 7 shows the hysteresis loops for three films with different seedlayer thickness, with the $(\text{Ti}_{4\text{nm}}/\text{Pt}_{0.5\text{nm}})$ seedlayer showing an almost doubling in coercivity.

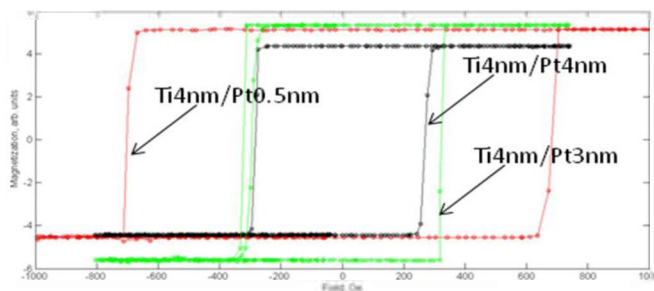


Fig. 3.7 Hysteresis loops of varying seedlayer thickness for Co/Pt

The first study incorporating Gd within the structure showed deterioration of performance. The graph in figure 8 shows the dependency of coercivity for the following system $\text{Ti}_{4\text{nm}}/\text{Pt}_{0.5\text{nm}}/[\text{Co}_{0.3\text{nm}}/\text{Pt}_{0.5\text{nm}}/\text{Gd}_x]_{x8}$.

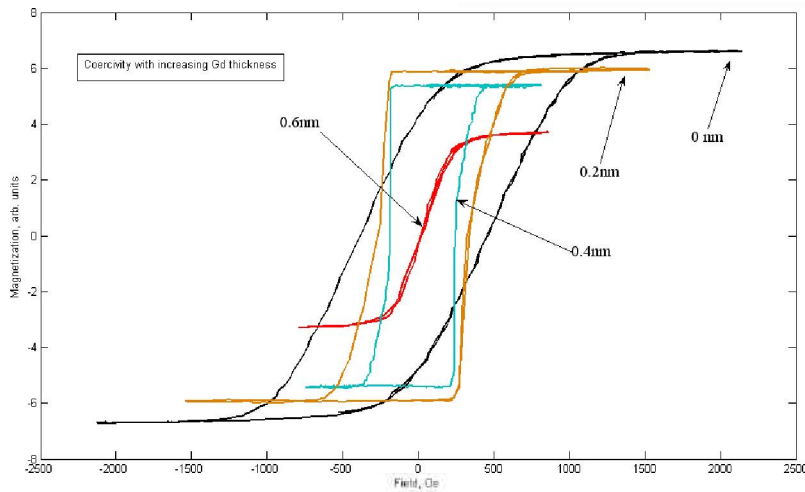


Fig. 3.8 Coercivity dependence with increasing Gd thickness within multilayer

At 0nm the coercivity is highest at around 700Oe, as the thickness of the Gd is increased to 0.2nm the coercivity reduces to ~ 400 Oe; however the squareness of the loop seems to improve. This is not readily expected and may point to a slight improvement in directionality of the magnetic anisotropy. The squareness and coercivity of the material is quickly diminished as the thickness is pushed beyond 0.4nm, and the multilayer becomes almost magnetically soft at a threshold of 0.6nm. A better explanation of this behavior is sought, and a study of the temperature effect can shed some light on this phenomena.

4. Continue collaborative work in order to better quantify and understand the role of f-electrons in observed and measured phenomena.
5. Quantify the effect and potential uses of using Gd in magnetic multilayered structures, and identify areas of future research work.

Milestone: Vertical stacking of media using Ti as decoupling layer was successful at a Ti thickness of 0.8nm.

Milestone: Vertical stacking of media using Gd as decoupling layer was successful at a Gd thickness of 1.5nm.

The framework chosen for incorporating Gd within multilayer structures was the stacking in the vertical dimension of magnetic perpendicular media based on the Co/Pd and Co/Pt systems. This requires a material system in-between the stacked layers that insulates the magnetic layers from each other, yet permits the growth of another multilayer system with perpendicular anisotropy. However, a thick exchange decoupling (i.e. insulating layer) has a negative effect on the perpendicular anisotropy; furthermore it will increase the effective magnetic thickness and noise within the media. Therefore, an

exchange decoupling layer that is thick enough to insulate the stack layers but thin enough to as to minimize the detrimental effects of an increasing overall thickness is sought. This was accomplished using both Ti and Gd suggesting that Gd may be viably integrated within these structures for purposes of sensing. The samples had the following structure:

- a. $Ti_{4nm}/Pt_{0.55nm}/[Co_{0.3nm}/Pt_{0.55nm}]_x4/Ti_{xnm}/Pt_{0.55nm}/[Co_{0.3nm}/Pt_{0.55nm}]_x7/Ti_{4nm}$
- b. $Ti_{4nm}/Pt_{0.55nm}/[Co_{0.3nm}/Pt_{0.55nm}]_x4/Gd_{xnm}/Pt_{0.55nm}/[Co_{0.3nm}/Pt_{0.55nm}]_x10/Ti_{4nm}$

Where the thickness of Ti was varied from 0.5nm to 4nm, and the thickness of Gd was varied from 0.5 to 3nm. The magnetic hysteresis loops for the Ti system can be seen in the figure 9. There was no noticeable difference in the coercivity of the samples with 4, 3, 2, and 1.5nm, and all showed distinct “kinks” in the magnetization loops, which indicate properly decoupled layers. When the Ti thickness was reduced to 0.8nm, the dual layers become coupled and the “kinks” disappear; whereas the 1nm thick Ti sample not only demonstrates exchange decouple behavior but also an increase in the coercivity of the bottom layer.

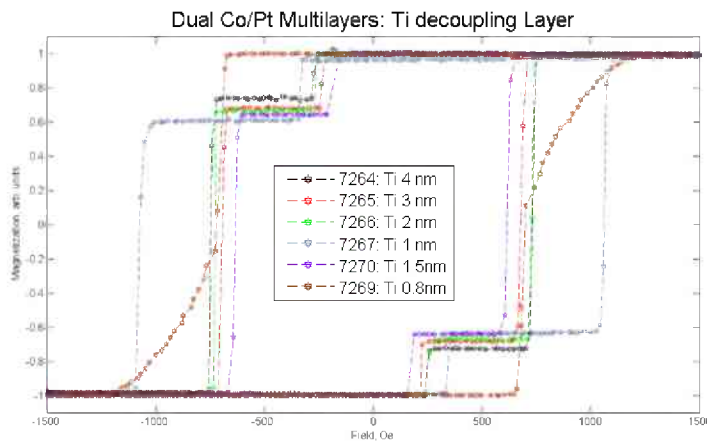


Fig. 3.9 Hysteresis loops investigating the minimum Ti decoupling thickness

In the case of Gd it was found that exchange decoupling is complete at 1.5nm and shows excellent separation between the two layers. The structures were designed to have different coercivity in order to clearly see two magnetically insulated layers. This is shown clearly in figure 10. The figure shows that the decoupling is complete and that the individual layers have smooth and intact hysteresis loops that are superimposed.

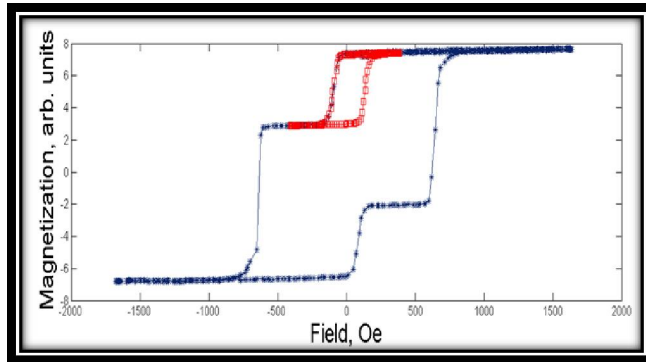


Fig 3.10 Two decoupled Co/Pt systems showing major and minor hysteresis loops

The results obtained with respect to use of Gd in multilayer magnetic structures indicate that incorporation of Gd within the multilayer stack has a negative effect on the magnetic properties. However, Gd seems to be an excellent candidate for the decoupling of stacked magnetic media. Future work that explores the temperature dependence of this behavior would be highly beneficial as Gd has a Curie temperature very close to room temperature. Gadolinium is unique for its high magnetic moment and for its special Curie temperature (above which ferromagnetism vanishes) lying just at room temperature, meaning it could be used as a magnetic component that can sense hot or cold. Furthermore, the electrical characterization of these structures in varying magnetic fields and under varying temperature may provide a more complete story as to how f-electron materials such as Gd affect the magnetic and electrical performance of magnetic multilayer structures.

Component II: Student Development and Support

Student Development

Two (2) Academic Assistants at the graduate level and four (4) undergraduates were funded simultaneously since September 29, 2006 until September 29, 2010. During the grant period a total of fourteen (14) undergraduates and (6) graduate students acquired research experience working under team members' guidance.

The Ph.D. students working in their dissertations on topics related to nuclear energy and their graduation date were: María Cotto (May 2009) and Eric Calderón (May 2011)

The stimulating environment developed by the program activities contributed to maintain a 100% retention rate among the participating students. The following undergraduate students completed their programs during the period: Ramon Polanco (BSME, May 2009), Jason Pérez (BSEE, May 2008), Rafael Colón (BSME, May 2008), Jessenia Marfisi (BS Chemistry, May 2008).

Summer internships

A total of eleven (11) students were sent to National Laboratories (LANL, SNL and LLNL), NNSA and DoE facilities. Twenty (21) undergraduate students participated in the 2010 Summer Internship at the Puerto Rico Energy Center (PREC).

As part of the no-cost extension activities, a special edition of the PREC Summer Internship Program took place from June 1st until July 31st, 2011 with the participation of 8 students under 6 mentors. The students were required to make a final presentation (in English) in an event held on August 19, 2011.

Support and dissemination

An international symposium addressing energy and nuclear energy topics was held four times since May 2007. It was jointly co-organized by the DSPMoE team with the PREC at the UT main campus with the participation of international speakers as well as federal and state agencies representatives. The purpose of the event was to stimulate research and professional interest in new and innovative technologies aligned with the DoE and the NNSA missions as well as for the dissemination of the UT DSPMoE program research activities and accomplishments among students, faculty members and professionals. The Symposia were held in May/June 31-1 (70 attendees), 2007; March 26-27 (85 attendees), 2008; April 30, 2008, (100 attendees); and May 13-14, 2010 (250 attendees)

All graduate and undergraduate students participating in the UT DSPMoE program were required to attend the four editions of the PREC International Conferences held in 2007, 2008, 2009 and 2010.

The following doctoral students and researchers made presentations during PREC International Conferences: María Maldonado (March 2009) Eric Calderón (March 2009) Rolando Roque (March 2009), Yazan Hijazi (March 2010).

“UT Distinguished Lecturer Series. . .” and other event

The “UT Distinguished Lecturer Series on Science, Technology and Engineering” was organized with the purpose of providing UT students and faculty members a wider perspective of the energy field. Since 2007 these events have taken place four times with the following speakers, dates and number of participants: Jose Colucci from University of Puerto Rico at Mayaguez (April 30th 2007, 50 students and 15 faculty members); Daniel Beltran from Valencia, Spain (April 30th 2008 - 80 students and 20 faculty members); Mr. David Ortiz from Ford Motor Company (June 17, 2009 - 60 students and 20 faculty members); Drs. Luis E. Fuentes and Maria E. Montero from the Advanced Materials Research Center, Chihuahua (Mexico June 17th, 2010 - 40 students and 12 faculty members)

All graduate and undergraduate students participating in the UT DSPMoE program were required to attend the four editions of the “UT Distinguished Lecturer Series on Science, Technology and Engineering” held in 2007, 2008, 2009 and 2010.

As part of the no-cost extension activities, a special seminar was held entitled “Challenges on Nuclear Security and a Close Look to the Fukushima Accident “ was held April 12, 2011. The speakers were Dr. Luis Edmundo Fuentes, Dr. Maria Montero, both from the Advanced Materials Research Center in Chihuahua, Mexico. The event attracted 99 participants (10 faculty members and 89 students).

Presentations from doctoral students

The following students and researchers made presentations during the UT Annual Researchers Conference: María Cotto (April 2007), Rolando Roque (March 2007), María Maldonado (March 2009),

Eric Calderón March 2009), R. Burgos (April 2009 and March 2010), E. Carpena (March 2010), Yazan Hijazi (March 2010) Rolando Roque (2010).

New and revised courses

A module on energy and nuclear energy topics was developed in 2006 and incorporated to all engineering programs as part of the Introduction to Engineering course (ENGI 100) with the purpose of increasing knowledge and motivating students to pursue energy studies. An average of 100 students enrolls in this course every fall semester and 100 students every spring. (25 undergraduate per course/ 4 sessions)

The doctoral level course Sustainable Energy and Environmental (ENSC 737) was revised in 2006 to incorporate more recent topics in energy and nuclear energy with the purpose of stimulating students' interest in these areas.

New and revised programs

The following UT academic programs were revised or created and implemented under the technical advice of the Massie Chair:

- Ph.D. in Environmental Sciences (new and later revised to satisfy the industry needs)
- MSc in Environmental Sciences (revised to satisfy the industry needs)
- MSc in Mechanical Engineering with concentration in Alternative Energy (new)
- BS in Industrial Management & Engineering (revised to fulfill the ABET requirements)
- BS in Civil Engineering including an environmental option (new)
- BS in Electrical Engineering (revised)
- Associate in Renewable Energy (new)

Research capabilities

The Puerto Rico Energy Center (PREC) has as part of its mission; the dissemination of scientific advances in Energy Research. It was originally named Plasma and Renewable Energy Center and was initiated by Dr. Roberto Lorán, as part of the Massie Chair Program efforts, as a proposal to the Center-Eastern Technological Initiative (known as INTECO from its Spanish acronym). It was adopted as a Strategic Initiative of INTECO operated by UT and has its own funding sources. An Executive Director integrated to the UT DSPMCoE team was appointed.

The PREC building was completed, and inaugurated on March 4th 2010 with the participation of local and federal government representatives. This new facility is primarily used by the UT DSPMCoE team. The DOE Massie Chair Program Officer and Supervisor along with the Massie Chairs from participating universities were in PR for a programmed meeting and participated in the ceremony.

Along the PREC building, a 1,250sf ecological house known as SOLARIA was donated and constructed by MiAntojo, Inc. The house serves as a laboratory for research, education, training and public awareness regarding renewable energy. This Center and the house leverage most of the UT DSPMCoE activities.

Another important aspect of the UT DSPMCoE program during this period was its contribution to strengthening the campus research infrastructure. Among the principal acquisitions of equipment funded by the DSMCoE program since May 2005 are the following: automatic surface area and

porosity analyzer, thermogravimetric analyzer, two vacuum lines, supercritical drying machine, CVD facility, manual hydraulic press, grinding machine and two furnaces located in the Materials Science Lab (ESL 207) of the School of Science and Technology; in the Materials Lab (SNL 147) the equipment is: GMW Electromagnet, Kepco power bipolar Supply, ATC Orion 4 Sputtering System, AJA CLC-75 chiller. In addition, an Advanced X-Ray Diffractometer was funded by a \$173,242 grant from the NSF Major Instrumentation program located in the PREC building. A \$500k contribution from SUAGM Central Administration was used to develop and implement the Bio-fuel laboratory also in the PREC building. All this equipment is benefiting not only the research activities of the program but also a variety of research projects at the Schools of Science & Technology and of Engineering as well as the PREC.

During the grant period, the DSPMCoE team has obtained additional funds not only to strengthen the capabilities of the two research projects and enhance the overall research infrastructure of UT. The Program served as a unique opportunity for other projects at UT to increase underrepresented minorities' participation in STEM related fields. In fact, by leveraging the aforementioned criteria and through the concerted effort of the UT DSPMCoE team and other UT researchers, 33 proposals were developed and submitted during the period of which 12 were approved in the amount of \$ \$1,931,306.

Due to its impact on the increase of campus research activities, special mention should be made of the involvement of the UT DSPMCoE team in the development, revision and implementation of the Strategic Research Plan for the institution.

Other student development activities

The Multidisciplinary Entrepreneurial Program for Innovation (MEPI) was initiated in March 2007 funded by a grant from the NSF PFI program with the purpose to promote entrepreneurial attitude and innovation spirit among students as well as to contribute to the development of their technical skills. Under this program seven (7) student run companies were established. As an example, EMCO, an enterprise supported by this grant and under the mentorship of the UT DSPMCoE team is involved in energy education and an energy efficiency campaign focused on students from elementary, to intermediate and high school. The program is being institutionalized supported by the institution and private donors.

Outreach

A special training program in energy topics was initiated at UT during the summer 2008 funded by INTECO (Central Eastern Technological Initiative Spanish acronym) WIRED program. It consisted of twenty hours of lecture and laboratory per week for a total of 50 hours. The course was offered in 2009 with the same funding source, in 2010 it became self-sustainable and looking forward to continue offering it regularly for engineering students and professional engineers of the Region.

As a result of the cooperation with other institutions participating in CIEMADeS a proposal entitled *Saturday Environmental Academy* was submitted to Environmental Protection Agency (EPA) under the leadership of Dr. Eddie Laboy. A \$39,297 proposal was approved for funding in October, 2006 and in a one year period was projected to benefit 250 high school students from Puerto Rico.

International cooperation

Caribbean countries are facing important environmental challenges. Sharing experiences and unifying strategies produce better results than isolated efforts. As an initiative of Dr. Roberto Lorán, several universities and other organizations (governmental and non-governmental) from Puerto Rico, the US Virgin Islands and other neighboring countries and territories established the International Center for Environmental Studies and Sustainable Development (CIEMADeS according to its Spanish acronym). The Center has its own funding sources and leverage most of the UT DSPMCoE activities.

The "International Conference of CIEMADeS" was celebrated by the first time in Santo Domingo, Dominican Republic, in August 10-12, 2005 (250 participants from 10 countries) and the second and third editions in November 3-5, 2006 (200 participants), and December 11-12, 2008 at UT main campus in Gurabo, Puerto Rico. In this two day biannual event, jointly organized by CIEMADeS and the UT DSPMCoE teams, speakers and presenters from the Caribbean Basin Countries and Islands addressed common environmental and energy related problems and solutions. The purpose of the UT DSPMCoE team's participation in this conference was to stimulate research and professional interest in new technologies and innovation aligned with DoE and NNSA missions as well as the dissemination of the program activities and accomplishments among students, faculty members and professionals. Also as a result of these events a number of international partnerships to pursue a variety of activities and projects were established.

Proposals submitted and funds received

During this period a total of 33 proposals were submitted and 12 of them approved. Funds were received for a total of \$1,931,306.

Year	PI/PD/ Author	Agency/Entity	Proposal Title
2006- 2007	Dr. José Ducongé	Higher Education Council	Certificación de Maestros de Física del Turabo
2007- 2008	Dr. José Ducongé	Higher Education Council	Mejoramiento Profesional de los Maestros de Física y Química
2008- 2009	Dr. José Ducongé	Higher Education Council	Mejoramiento Profesional de los Maestros de Física y Química
2008- 2009	Dr. José Ducongé	NSF	Creation of an X-ray Diffraction, Raman Spectrometry and Adsorption Materials Characterization CyberLab
2009- 2010	Dr. José Ducongé	Higher Education Council	Mejoramiento Profesional para Maestros de Ciencia: Energía y Ambiente (MPM:CEA)
2006- 2007	Dr. Roberto Loran	DOE	Universidad del Turabo Massie Chair of Excellence
2006- 2007	Dr. Roberto Loran	NSF	UT Partnership for Innovation - Hispanic Enterprise Program for Innovation (PIP/HEPI)
2006- 2007	Dr. Roberto Loran	AMGEN Foundation	College Ambassador Program
2007- 2008	Dr. Roberto Loran	DOE	Universidad del Turabo Massie Chair of Excellence
2007- 2008	Dr. Roberto Loran	NSF	UT Partnership for Innovation - Hispanic Enterprise Program for Innovation (PIP/HEPI)
2007- 2008	Dr. Roberto Loran	NSF/Syracuse University	CNY, Caribbean, Hopkins AGEP Alliance

2007-2008	Dr. Roberto Loran	NSF	UT Center for Research Excellence in Science and Technology for Sustainable Energy
2007-2008	Dr. Roberto Loran	Syracuse University/NSF	CNY, Caribbean, Hopkins AGEP Alliance
2008-2009	Dr. Roberto Loran	DOE	Universidad del Turabo Massie Chair of Excellence
2008-2009	Dr. Roberto Loran	NSF	UT Partnership for Innovation - Hispanic Enterprise Program for Innovation (PIP/HEPI)
2008-2009	Dr. Roberto Loran	NSF	International Workshop on Logistics and Port Engineering and its Impact on Research and Education in the Americas
2009-2010	Dr. Roberto Loran	DOE	Universidad del Turabo Massie Chair of Excellence
2009-2010	Dr. Roberto Loran	DOE	UT/GTKS Training Program Development for Commercial Buildings Equipment Technicians
2009-2010	Dr. Roberto Loran	DOE	UT/GTKS Training Program Development for Energy Commissioning Agents/Auditors
2009-2010	Dr. Roberto Loran	DOE	UT/GTKS Training Program Development for Commercial Building Operators
2009-2010	Dr. Roberto Loran	DOE	DOE Massie Chair of Excellence in Environmental Disciplines: Nuclear Defense Nonproliferation & Energy Stewardship Initiative II
2010-2011	Dr. Roberto Loran	PR Science, Tech & Rsrch Trust	Primer Simposio de Energia Sustentable

2010-2011	Dr. Roberto Loran	PR Science, Tech & Rsrch Trust	Electrical Interconnection of the Caribbean Conference
2006-2007	Dr. Rolando Roque	NSF	Ammonia Adsorption in High Specific Surface Area Nanoporous Silica Materials for Hydrogen Storage
2006-2007	Dr. Rolando Roque	DOE	Ammonia Adsorption in High Specific Surface Area Nanoporous Silica Materials for Hydrogen Storage
2007-2008	Dr. Rolando Roque	NSF	Ammonia Adsorption in Nanoporous Silica Materials for Hydrogen Storage and Other Applications
2007-2008	Dr. Rolando Roque	NASA	UT-NASA-Research Center for Multiscale Systems (UT-NASA-RCMS)
2008-2009	Dr. Rolando Roque	NSF	Universidad del Turabo Center of Research Excellence in Science and Technology for Sustainable Energy Systems (UT-CREST-SES)
2008-2009	Dr. Rolando Roque	NASA	NASA Universidad del Turabo Research Center for Multiscale Systems (NASA-UT-RCMS)
2009-2010	Dr. Rolando Roque	NSF	MRI-R2: Acquisition of an XRD, Raman Spectrometer and Sorption Analyzer for the Creation of a Materials Characterization Cyberlab
2009-2010	Dr. Rolando Roque	NSF	Theoretical Calculation & Experimental Measurement of the Adsorption Enthalpy of Methane in Modified Vertically-Aligned SWCNTs & its Relation with Methane Storage
2009-2010	Dr. Rolando Roque	NSF	Research of the Decomposition of organic Compounds in Water Solution by the Mechanical Activation of Semiconductor Catalysts
2010-2011	Dr. Rolando Roque	NSF	Research Study of the Adsorption Space of Tuned Vertically-Aligned Single Walled Carbon Nanotubes Bundles and its Relation with Methane Storage

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2. R. Roque-Malherbe, Physical Chemistry of Materials: Energy and Environmental Applications, CRC Press, Boca Raton, FL, USA, 2009, **Book**.
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15. Y. Hijazi, E.B. Svedberg, T. Heinrich, S. Khizroev, "Comparative Corrosion Study of Binary Oxide and Nitride Overcoats Using In-Situ Fluid-Cell AFM" *Journal of Materials Characterization, Materials Characterization*, Volume 62, Issue 1, Pages 76–80 (01/2011).
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2. Y. Hijazi, Raymond Burgos, Armando Vasquez, "Effect of Deposition Parameters on interface quality in Multiayered structures.", UT Researchers Forum, April 2009.
3. Raymond Borgus, Emmanuel Carpena, Yazan Hijazi, "Multilevel magnetic media, latest results: Stacked Multilayers" UT Researchers Forum, March 12, 2010.
4. Emmanuel Carpena, Raymond Borgus, Yazan Hijazi, "Development of in-house Kerr microscopy magnetic characterization tool: Design and Progress" Presentation at the VIII UT Researchers Forum, March 12, 2010.

5. Mechanocatalytic Decomposition of Phenol by: R. Roque-Malherbe, M. C. Cotto, S. Nieto and J. Duconge. This paper was presented in the IUPAC-XXVIII Latin American Congress of Chemistry. This paper was presented in the IUPAC-XXVIII Latin American Congress of Chemistry (2007).

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