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13. ABSTRACT *(Maximum 200 words)*

The specific aim of this research project is the development of novel methods for preparing improved catalysts for direct methanol fuel cells (DMFCs). These catalysts consist of metal alloy nanoclusters dispersed onto a conductive carbon support. Synthetic control of the alloy nanocluster composition is achieved by preparing molecular precursors in which the precursor contains two or more metals of a desired stoichiometry. Adsorption of single-source molecular precursors onto Vulcan carbon powder followed by appropriate thermal treatment affords metal alloy or intermetallic/carbon nanocomposites having thirteen different binary compositions and one ternary composition. Tests performed in an operating DMFC indicate that the catalytic activity of two PtRu/Vulcan carbon nanocomposites as anode catalysts is superior to that of a similar commercial PtRu/Vulcan carbon catalyst. A rapid synthesis of such binary alloy/Vulcan carbon nanocomposites using microwave heating has been discovered. Preliminary attempts to prepare passivated metal nanoclusters suitable for size selection are also discussed. The preparation of an unrelated cobalt/fullerene nanocomposite is included for completeness.

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(1) Foreword

This document serves as the Final Progress Report for the first three-year grant awarded to the Principal Investigator by the ARO to pursue new synthetic strategies for the preparation of catalysts for direct methanol fuel cells. While selected results of this investigation are summarized below, it is important to note that additional support of this study was provided by the ARO through a DURIP grant that permitted the purchase of a powder XRD facility and through an AASERT grant that provided salary support for selected participants of this research project.

(2) Table of Contents

(3) Statement of the Problem Studied

One research objective of the Army Research Office is the development of improved catalysts for the oxidation of methanol in direct-methanol-fuel-cells (DMFCs). Practical DMFCs would be attractive compact power sources for electrical power production. Current wisdom dictates that crystalline metal alloy nanoclusters of particular compositions should be highly active catalysts for methanol oxidation. To minimize the unit cost of metal, these alloy particles should be supported on an electrically conducting carbon powder (such as Vulcan carbon) forming a nanocomposite catalyst.

The research hypothesis being investigated in this project is the following: Can molecules serve as single-source precursors to crystalline binary intermetallic or alloy nanoparticles supported on Vulcan carbon powder? More specifically, molecules containing a precise stoichiometry of two or more different metals might serve as precursors to crystalline nanoclusters of metal alloy having the same metal stoichiometry. Because metal alloy/carbon nanocomposites are known to be active as DMFC anode catalysts, better control of the metal alloy stoichiometry at the nanoparticle scale might afford DMFC anode catalysts having higher activity. The activity of DMFC anode catalysts might also be improved through better control of metal catalyst particle size or of thermal treatment conditions. Selected investigation of these other aspects relating to catalyst activity has also been undertaken during this project period.

(4) Summary of the Most Important Results

As listed in Table I, twenty-one carbon-supported nanocomposites have been prepared from single-source molecular precursors, characterized by several methods, and submitted for DMFC testing (nineteen of the twenty-one nanocomposites) during the project period. Compounds used as single-source precursors included known complexes (1, 2, 3, 4, 7, 12, 13, and 16), new but not particularly novel complexes (5, 6, 8, 11, 14, and 15), or novel complexes (9 and 10). The core structure or metal content of the molecular precursor is designed to have the precise elemental stoichiometry desired of the resulting nanocluster substance except in two instances. The metal content of precursor 9 is $Pt_3Hg_2Ru_2$, as is evident from the x-ray crystal structure of complex 9 (see Figure 1). However, TGA analysis of this complex reveals sharp loss of the mercury atoms in a single mass-loss event. Thermal treatment of complex 9/Vulcan carbon composites shows a similar loss of the mercury content and formation of the expected Pt_3Ru_2/Vulcan carbon nanocomposite. Secondly, precursor 5 has a ternary metal phosphide content of $Pt_1Ru_1P_1$. Formation of the $Pt_1Ru_1P_2$/Vulcan carbon nanocomposite using this precursor requires the addition of a equimolar amount of free PPh_3 prior to thermal treatment.

The resulting nanocomposite catalysts are characterized typically by TEM, electron diffraction, EDS, XRD and elemental microanalysis. Experience in preparing and characterizing these nanocomposites greatly improves the purity of the active catalyst phase. Much of the progress in synthesizing pure nanocomposites occurred following the acquisition of a Scintag powder XRD system having a high-temperature attachment. Precursor/Vulcan carbon composites are subjected to pre-programmed alteration of thermal treatment and reactive/inert gas environment while acquiring real-time XRD scans. Conditions favoring the formation of unwanted products or metal phase separation can, therefore, be avoided. Programmable tube furnaces are used for bulk syntheses.

Table I. Metal Alloy/Carbon Nanocomposites Prepared During Grant Period

Metal Alloy Composition	Sample No.	Total M wt. %	Ave. Dia. (nm)	Molecular Precursor[a]	Submitted for Testing
Co_3C	SBM126	13	< 20	$HCCo_3(CO)_9$, **1**	yes
Pt_1Sn_1	SBM117	20	6	$[(Ph)(Ph_3P)_2PtSnPh_2Cl]$, **2**	yes
Pt_1Sn_1	DK167	35	18	$[(Cl)(Et_3P)_2PtSnCl_3]$, **3**	yes
Pt_3Sn_1	SJ50-01	16	8	$[Pt_3(dppm)_3(CO)(SnF_3)][PF_6]$, **4**	yes
Pt_1Ru_1	WDK021	10	3.6	$[(C_{10}H_{16})RuPtCl_4(PPh_3)]$, **5**	yes
	WDK025	32	3.9	$[(C_{10}H_{16})RuPtCl_4(PPh_3)]$, **5**	yes
	WDK020	35	2.8	$[(C_{10}H_{16})RuPtCl_4(PPh_3)]$, **5**	yes
	WDK047	50	3.7	$[(C_{10}H_{16})RuPtCl_4(PPh_3)]$, **5**	yes
	WDK089	39	2.6	$[(C_{10}H_{16})RuPtCl_4(C_2H_4)]$, **6**	yes
	DB3-11	20	3	$[(C_{10}H_{16})RuPtCl_4(C_2H_4)]$, **6**	yes
	JDC01-022-1	26	3.9	$[Cl_2Pt(C_8H_6N_4)Ru(C_{10}H_8N_2)_2][PF_6]_2$, **7**	yes
	JDC02-004	40	1.8	$[Cl_2Pt(C_8H_6N_4)Ru(C_{10}H_8N_2)_2][BF_4]_2$, **8**	yes
Pt_3Ru_2	WDK065	25	3.9	$[Pt_3(dppm)_3\{HgRuCp(CO)_2\}_2][PF_6]_2$, **9**	no
Pt_3Ru	SBM153	22	9	$[Pt_3(dppm)_3RuCp][PF_6]$, **10**	yes
Pt_3Ru	JDC01-093	37	5.7	$[Ru(C_{18}H_{12}N_4PtCl_2)_3][BF_4]_2$, **11**	yes
$PtMo_2$	KCK137	50	13	$Ptpy_2[MoCp(CO)_3]_2$, **12**	yes
$PtMo$	KCK178	52	3.9	$Pt(COD)(Me)[MoCp(CO)_3]$, **13**	no
Pt_3Mo	SBM146	22	4	$[Pt_3(dppm)_3MoCp(CO)][PF_6]$, **14**	yes
Pt_3Mo	KCK114	30	3.4	$[Pt_3(dppm)_3MoCp(CO)][BPh_4]$, **15**	no
Ru_1Mo_1	KCK073	45	1.5	$[(C_7H_7)(OC)_3MoRuCp(CO)_2]$, **16**	yes
$Pt_1Ru_1P_2$	WDK090	40	3.6	$[(C_{10}H_{16})RuPtCl_4(PPh_3)]$, **5**	yes

[a] $dppm = Ph_2PCH_2PPh_2$; $Cp = \eta^5\text{-}C_5H_5$; $COD = 1,5$-cyclooctadiene; $py =$ pyridine; $C_{10}H_{16} = \eta^3:\eta^3$ -2,7-dimethyloctadienediyl; $C_8H_6N_4 =$ bipyrimidine; $C_{10}H_8N_2 = 2,2'$-bipyridine; $C_{18}H_{12}N_4 = 2,3$-bis(2-pyridyl)quinoxaline; $C_2H_4 =$ ethylene

The Co_3C, Pt_1Sn_1, and Pt_3Sn_1/Vulcan carbon nanocomposites were prepared as a "proof of concept" to validate the synthetic strategy. Each of these crystalline nanocomposites are intermetallic substances having a unique XRD pattern. In each case, the formation of nanoclusters having the desired elemental stoichiometry is confirmed by matching experimental and standard XRD scans. The Pt-Ru/Vulcan carbon nanocomposites were targeted as compositions most likely to perform as DMFC anode catalysts of highest activity, while the Pt-Mo/Vulcan carbon nanocomposites were prepared as possible PEM/DMFC catalysts having high CO-tolerance. Dr. Murphy of Lynntech, Inc., requested that we synthesize a RuMo/Vulcan carbon nanocomposite as a DMFC cathode catalyst which might exhibit high methanol tolerance. As an unexpected discovery, a $Pt_1Ru_1P_2$/Vulcan carbon nanocomposite can be prepared from precursor **5** and excess triphenylphosphine. The structure and composition of this ternary mixed-metal phosphide is confirmed by full-profile fitting of the XRD pattern using Rietveld refinement. Similar refinements have been applied to XRD scans of several of the above binary metal alloy nanocomposites, as well.
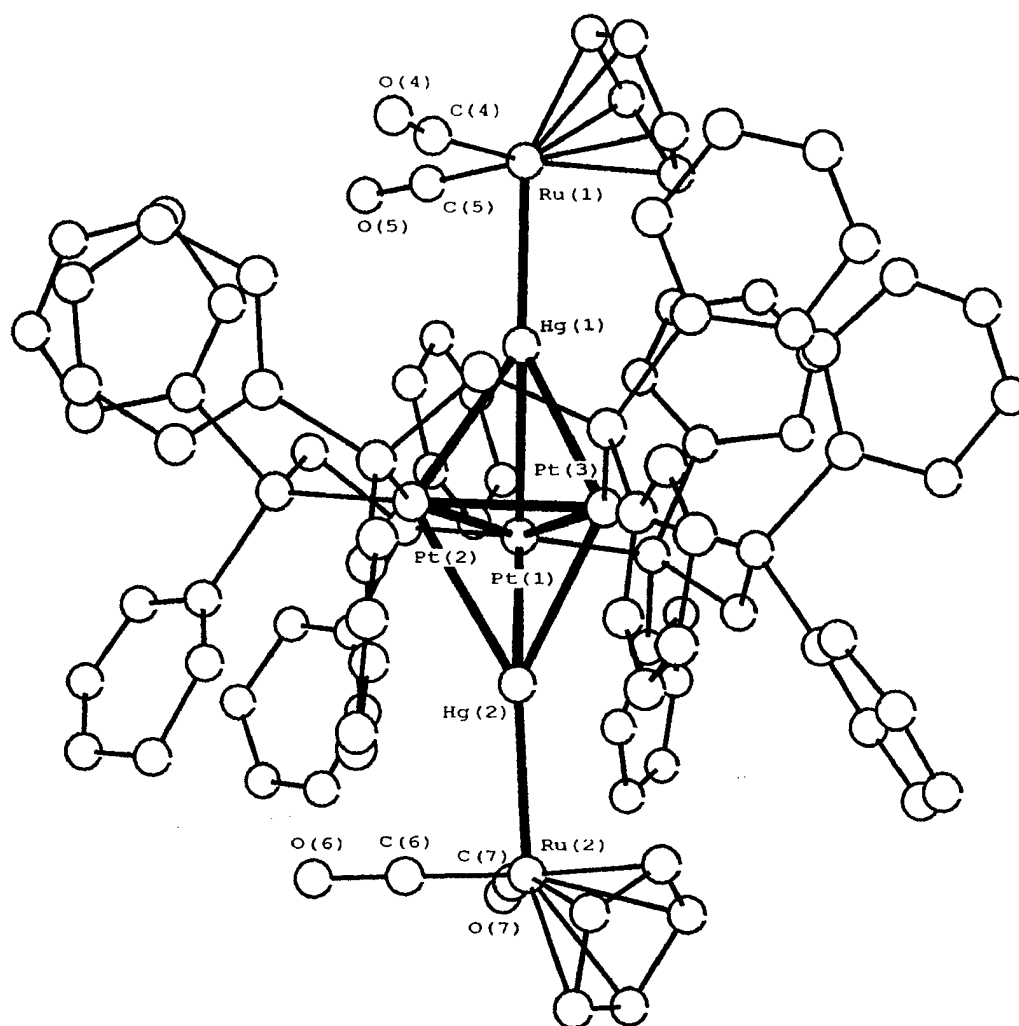
Figure 1. The molecular structure of the cation of complex 9. Hydrogen atoms have been omitted.

The successful synthesis of Pt-Ru binary alloy nanocomposites of controlled alloy stoichiometry is of particular importance to the development of improved anode catalysts for DMFC applications. As shown in Table II, two Pt_1Ru_1/Vulcan carbon nanocomposites, one Pt_3Ru_2/Vulcan carbon nanocomposite, and one Pt_3Ru_1/Vulcan carbon nanocomposite have been prepared from designed single-source molecular precursors. Each of these nanocomposites exhibit average metal alloy nanocluster sizes of interest for DMFC catalyst applications and, most importantly, exhibit fcc cell constants consistent with the cell constants expected for Pt-Ru alloys of these compositions.

However, due to the similar atomic radii for Pt and Ru atoms, the values of the fcc cell constants for Pt-Ru alloys is not a particularly sensitive parameter for evaluating alloy composition. Other techniques involving diffraction or absorption methods, such as EXAFS experiments, also provide only average compositional information due to the relatively large size scale interrogated by these methods. To obtain direct measurement of individual Pt-Ru nanocluster stoichiometries, we have initiated a collaboration with Dr. Ed Kenik of ORNL. Using FEG TEM instrumentation at ORNL and through travel support provided by the SHaRE ORISE program, we are now able to acquire EDS spectra for individual Pt-Ru nanoclusters within our catalyst samples. These data also permit a determination of the compositional variation in metal alloy stoichiometry from particle to particle within a sample. To date, such truly "on-particle" EDS data have been acquired on three

Table II. Summary of Selected Pt-Ru/Vulcan Carbon Nanocomposites Prepared During Grant Period

Metal Alloy Composition	Molecular Precursor	Total M wt. %	Ave. Dia, (nm) (XRD/TEM)	fcc a_{obs} (Å)	fcc $a_{expected}$ (Å)
Pt_1Ru_1	6	39	2.7/2.6	3.858(6)	3.864
Pt_1Ru_1	8	33	4.2/4.3	3.86(1)	3.864
Pt_3Ru_2	9	25	7.5/3.9	3.875(2)	3.876
Pt_3Ru_1	11	37	6.7/5.7	3.911(1)	3.895

Pt-Ru catalysts prepared using single-source molecular precursors. While data analysis is currently in progress, initial results look very promising. Each metal alloy nanocluster stoichiometry is very close to the bulk alloy stoichiometry given the precision of the measurement. Details of this analysis will be presented in future publications and technical reports.

During this grant period, several of the above nanocomposites have been evaluated as DMFC anode catalysts either electrochemically or in working DMFCs. These testing results have been provided by Dr. Oliver Murphy of Lynntech, Inc., or by Dr. Gene Smotkin of Illinois Institute of Technology. DMFC testing results have also been obtained in a recently established collaboration with Drs. Smyrl and Shores at the University of Minnesota. Unfortunately, more testing results are available on our first- or second-generation catalyst samples than have been obtained on our third-generation catalysts. Hopefully, testing results will be forthcoming on these most recently prepared nanocomposites.

In general, PtSn alloys have lower catalytic activity for methanol oxidation than do Pt/Ru alloys. This result is expected based on the experience of others. The Co_3C/Vulcan carbon nanocomposite was inactive as a DMFC anode catalyst. This result was also expected based on published results reporting the activity of this substance only at temperatures above 200°C; however, the activity of nanocomposite SBM126 prepared from a single-source molecular precursor was evaluated to determine if this synthetic strategy might provide a more active catalyst. The RuMo/C nanocomposite (KCK073) was examined as a possible DMFC cathode catalyst that might exhibit some degree of methanol tolerance, but results were disappointing.

However, selected PtRu/C nanocomposites tested well as DMFC anode catalysts. In Figure 2, the i-V curves are shown for the Pt_1Ru_1/Vulcan carbon nanocomposites JDC01-022-1, WDK025, WDK047, and a commercial E-TEK Pt_1Ru_1/C nanocomposite when these nanocomposites are tested as DMFC anode catalysts at the same loading. The specific testing conditions are the same as those reported in previous Progress Reports. The cathode catalyst is 2 mg/cm^2 unsupported Pt black, the methanol concentration is 2 M, and the cell temperature is 80°C. These results were obtained at Lynntech, Inc.

While the nanocomposite WDK047 is less active at all potentials than the commercial E-TEK catalyst, the other two nanocomposites had greater activity. Nanocomposite JDC01-022-1 has the highest activity for methanol oxidation at open circuit and at low current densities of all the samples tested, including the commercial E-TEK catalyst. In addition, nanocomposite WDK025 clearly outperformed all of the catalysts tested at all higher current densities. At an anode potential of 0.4 V, the current density produced by this nanocomposite approaches 800 mA/cm^2.
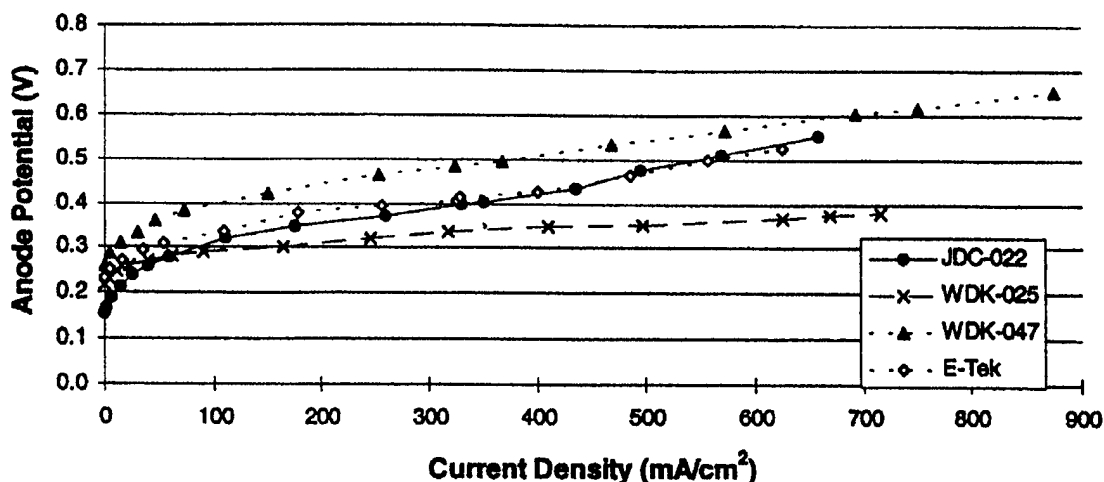
Figure 2. Comparison of i-V curves for the Pt_1Ru_1/C nanocomposites JDC01-022-1, WDK025, WDK047, and the commercial E-TEK Pt_1Ru_1/C nanocomposite as DMFC anode catalysts at the same loading. The cathode catalyst is 2 mg/cm^2 unsupported Pt black, the methanol concentration is 2 M, and the cell temperature is 80°C.

These testing results are very encouraging. We anticipate that our third-generation nanocomposites will exhibit even higher activity for methanol oxidation.

PtRu/Vulcan Carbon Nanocomposites of Narrow Particle-Size Distribution

An ideal synthetic route to DMFC catalysts would afford metal nanocrystals of uniform size with synthetic control over that size. In practice, narrow particle-size distributions would be acceptable.

In our "molecules-to-nanocluster" synthetic strategy for preparing metal or metal alloy nanocomposites on Vulcan carbon, a thermal treatment period extending typically over 2 - 3 hours is employed. During that time, nanocluster growth presumably occurs by diffusion mechanisms giving monomodal nanoparticle-size distributions of significant breadth (typically 3 - 4 nm full-width-at-half-height). Smaller, and perhaps more uniform, nanoparticles would be formed if molecular degradation and nanoparticle growth could be accomplished more rapidly and with better control of thermal annealing.

We recently initiated a novel modification of our metal/carbon nanocomposite synthetic procedure to achieve more control over nanocluster growth. Vulcan carbon was found to be rapidly heated through microwave irradiation by dielectric loss. A vial containing Vulcan carbon becomes hot enough to soften glass after only brief irradiation (ca. 60 s) in a conventional microwave oven.

Deposition of Pt_1Ru_1 molecular precursor **6** onto Vulcan carbon followed by microwave irradiation under appropriate gaseous atmospheres over a total heating period of less than 60 seconds gives the expected $Pt_1Ru_1/$carbon nanocomposite. A TEM micrograph of such a nanocomposite is shown in Figure 3. Particle contrast is consistent with crystalline PtRu nanoclusters. A histogram of PtRu nanoparticle diameters reveals an average nanocluster diameter of 3.2 nm with a standard deviation of 0.66 nm and a size distribution of only ca. 1.4 nm at full-width-at-half-height. The Pt_1Ru_1

Figure 3. TEM micrograph of a PtRu/Vulcan carbon nanocomposite prepared by microwave heating.

nanoclusters give a diffraction pattern consistent with a fcc cell exhibiting broad peaks as expected from the small average particle size of the Pt_1Ru_1 nanoclusters. Peak positions give a fcc lattice parameter of 3.867 Å which is the same within error to that obtained for Pt_1Ru_1/Vulcan carbon nanocomposites prepared from the same molecular precursor but heated in a conventional tube furnace (3.866 Å). Taken together, these results indicate that an exciting new route to metal/carbon nanocomposites has been discovered. Further refinement of this procedure should give more narrow metal nanocluster size distributions on the bulk scale.

One Pt_1Ru_1/Vulcan carbon nanocomposite prepared by microwave heating has been tested as a DMFC catalyst. Although this sample was active as a DMFC anode catalyst, its activity was less than that expected and less than that of a comparable commercial E-TEK, Inc., catalyst. This result was unexpected but possibly indicates that such short-term thermal treatments might not produce clean alloy surfaces when precursors containing chlorine are used. Chlorine, bromine, and iodine are known poisons for Pt-Ru alloy surfaces. Pt-Ru/Vulcan carbon nanocomposites will be prepared by microwave heating using either longer reductive thermal treatment or precursors lacking chlorine to better evaluate the DMFC activity of catalysts prepared by this novel method.

Metal Nanocluster Sols for Size Selection

Nanoclusters prepared by conventional thermal decomposition/annealing processes like those described above are usually quite polydisperse in particle size. Size distributions of 3 - 4 nm at full-width-at-half-height or larger are not uncommon. While synthetic routes to quite monodisperse nanoclusters are available for nano-CdSe and for Au nanoclusters, a general method for achieving nanocluster size selection remains elusive, especially for metal nanoclusters. Application of relatively simple size selection methods, such as centrifugation, fractional precipitation, or gel permeation chromatogaphy, require stable colloidal nanocluster solutions. Furthermore, testing nanocrystal catalytic activity, as in DMFCs, as a function of catalyst particle size requires size selection on a bulk scale not just on the analytical scale.

During this grant period, we initiated a novel approach for achieving metal nanocluster size selection on a bulk scale that retains our "molecules-to-nanocluster" synthetic strategy. Molecular precursors are physisorbed or deposited onto selected powdered substrates that are water soluble. Thermal treatment of these molecularly doped powders under proper conditions gives nanocomposites containing metal nanoclusters on a water-soluble support. Dissolution of the solid support in water affords a salt-stabilized colloidal solution of metal nanoclusters. Under appropriate conditions, inorganic cations are removed from these aqueous colloidal solutions using dialysis. Surface-passivating agents are added to the dialysate to stabilize the metal nanoclusters against irreversible agglomeration during solvent evaporation and to prepare the metal nanoclusters for conventional size selection procedures.

We have tested this strategy for "proof of concept" using Ph_3PAuCl as a molecular precursor to Au nanoclusters. Thermal decomposition of this molecular precursor on nine different water-soluble solid supports occurs to give salt-stabilized Au colloids upon dissolution in water. These colloids successfully undergo de-salting by dialysis. The degree to which these Au nanoclusters can be surface-passivated for successful size selection is under study.

Preparation of a Co/Fullerene Nanocomposite for Hydrogen Storage

In collaboration with Dr. Raouf Loutfy of MER Corporation, we undertook a preliminary study of the practicality of synthesizing a specific type of Co/fullerene nanocomposite. The desired nanocomposite consists of a spherical particle of cobalt metal coated with a concentric layer of fullerenes. Cobalt carbonyl compounds were chosen as precursors to Co metal nanoparticles, and decomposition of these precursors in the presence of fullerenes yielded a Co/fullerene nanocomposite material. The results of this study will be submitted for publication.

(5) List of all Publications, Technical Reports, and Technical Presentations

Publications:

(a) "Nanoclusters of Silicon and Germanium," William. D. King, Deborah. L. Kunkel, and Charles M. Lukehart, **J. Cluster Sci., 1997**, *8*, 267 - 292.

(b) "Organometallic Compounds as Single-Source Precursors to Nanocomposite Materials: An Overview," Joseph P. Carpenter, C. M. Lukehart, Stephen B. Milne, S. R. Stock, James E. Wittig, Bobby D. Jones, Robert Glosser, and Jane G. Zhu, **J. Organomet. Chem., 1998**, *557*, 121 - 130.

(c) "Nanocomposites Containing Nanoclusters of Ag, Cu, Os, Pd, Pt, Re, or Ru in a Silica Xerogel Matrix," Joseph P. Carpenter, C. M. Lukehart, Stephen B. Milne, D. O. Henderson, R. Mu, S. R. Stock, and James E. Wittig, **Chem. Mater., 1997**, *9*, 3164 - 3170.

(d) "Formation of Crystalline Nanoclusters of Fe_2P, RuP, Co_2P, Rh_2P, Ni_2P, Pd_5P_2, or PtP_2 in a Silica Xerogel Matrix from Single-Source Molecular Precursors," C. M. Lukehart, Stephen B. Milne, and S. R. Stock, **Chem. Mater., 1998**, *10*, 903 - 908.

(e) "Synthesis and Molecular Structure of the Mercury-Bridged Heteronuclear Complex $[Pt_3(dppm)_3\{\mu_3\text{-Hg-RuCp(CO)}_2\}_2][PF_6]_2$," William D. King and Charles M. Lukehart, **J. Cluster Sci., 1998**, *9*, 107 - 121.

(f) "Nanocomposites Prepared by Sol-Gel Methods: Synthesis and Characterization," Krzysztof C. Kwiatkowski and C. M. Lukehart, Contribution in **"Handbook of Nanostructured Materials and Nanotechnology,"** H. S. Nalwa, Ed., Academic Press, in press.

Technical Reports:

(a) "ARO Interim Progress Report," 1 May 1995 - 31 December 1995.

(b) "ARO Interim Progress Report," 1 January 1996 - 31 December 1996.

(c) "ARO Interim Progress Report," 1 January 1997 - 31 December 1997.

Technical Presentations:

"Nanocomposites Containing Nanoclusters of Selected First-Row Transition Metal Phosphides," C. M. Lukehart, Stephen B. Milne, S. R. Stock, Robert D. Shull, and James E. Wittig, Invited Paper at the American Chemical Society, Fall National Meeting, August, 1995, Chicago, IL.

"Nanocomposites From Molecularly Doped Silica Xerogels: An Overview," Joseph P. Carpenter, C. M. Lukehart, Stephen B. Milne, S. R. Stock, James E. Wittig, Bobby D. Jones, R. Glosser, Donald O. Henderson, R. Mu, Robert D. Shull, Jane G. Zhu, and Z. U. Rek, Invited Paper at the Society for the Advancement of Material and Process Engineering, SAMPE Technical Conference, October, 1995, Albuquerque, NM.

"Nanocomposites Containing Nanoclusters of Rhenium or Ruthenium," Stephen B. Milne and C. M. Lukehart, American Chemical Society, Southeast/Southwest Joint Regional Meeting, November, 1995, Memphis, TN.

"Novel Synthetic Routes to Nanocomposites of Transition Metal Phosphides," Charles M. Lukehart and Stephen B. Milne, James E. Wittig, Stuart R. Stock, and Robert D. Shull, American Chemical Society, Spring National Meeting, March, 1996, New Orleans, LA.

"Preparation of Nanocomposites Containing Nanoclusters of Transition Metals," Charles M. Lukehart, Stephen B. Milne, James E. Wittig, Stuart R. Stock, Joseph P. Carpenter, and Zofia U. Rek, American Chemical Society, Spring National Meeting, March, 1996, New Orleans, LA.

"Novel Synthetic Routes to Nanocomposites of Transition Metal Phosphides," Charles M. Lukehart and Stephen B. Milne, James E. Wittig, Stuart R. Stock, and Robert D. Shull, American Chemical Society, Spring National Meeting, March, 1996, New Orleans, LA. [Paper chosen for the Special Sci-Mix Session]

"Synthesis of Pt Quantum Dots in SiO_2 Xerogel for Nonlinear Optical Studies," K. Warren, R. Haglund, C. M. Lukehart, and D. Osborne, A Mini-Symposium on Frontiers of Materials Research, May, 1996, Vanderbilt University, Nashville, TN.

"Novel Synthetic Routes to Nanocomposites of Transition Metal Phosphides," Charles M. Lukehart and Stephen B. Milne, James E. Wittig, Stuart R. Stock, and Robert D. Shull, A Mini-Symposium on Frontiers of Materials Research, May, 1996, Vanderbilt University, Nashville, TN.

"Nanocomposites Containing Nanoclusters of the Transition Metal Phosphides Fe_2P, Co_2P, or Ni_2P," C. M. Lukehart, S. B. Milne, and S. R. Stock, Fifth Annual Workshop of the Consortium for Nanostructured Materials, October, 1996, Vanderbilt University, Nashville, TN.

"Synthesis of Pt Quantum Dots in SiO_2 Xerogel for Nonlinear Optical Studies," K. Warren, R. Haglund, C. M. Lukehart, and D. Osbourne, Fifth Annual Workshop of the Consortium for Nanostructured Materials, October, 1996, Vanderbilt University, Nashville, TN.

"From Molecules to Nanocomposites - Particles Much Smaller than the Wavelength of Visible Light," C. M. Lukehart, Local American Chemical Society lecture, Northern Kentucky/Indiana Border Section, November, 1996, Owensboro, KY.

"Organometallic Compounds as Single-Source Precursors to Nanocomposite Materials: An Overview," Joseph P. Carpenter, C. M. Lukehart, Stephen B. Milne, Frank E. Jones, III, S. R. Stock, James E. Wittig, Bobby D. Jones, Robert Glosser, Donald O. Henderson, R. Mu, and Jane G. Zhu, Second Journal of Organometallic Chemistry Conference, April, 1997, San Francisco, CA.

"Nanocomposites from Single-Source Molecular Precursors," C. M. Lukehart, Sixth Annual Workshop of the Consortium for Nanostructured Materials, October, 1997, University of Kentucky, Lexington, KY.

"Synthesis of a Heteronuclear Cluster Containing Pt, Ru and Hg and the Preparation of Carbon-Supported Metal Nanoparticles from this Molecular Precursor," William D. King and Charles M. Lukehart, American Chemical Society, 215th National Meeting, March. 1998, Dallas, TX.

"Preparation of Carbon-Supported Bimetallic and Alloy Phase Nanocrystals Using Single-Source Molecular Precursors," Deborah L. Boxall, James D. Corn, and Charles M. Lukehart, American Chemical Society, 215th National Meeting, March. 1998, Dallas, TX.

"Nanocomposite Materials Using Single-Source Molecular Precursors," Charels M. Lukehart, Dow Chemical Company, June 1998, Midland, MI.

"Preparation of Gold Nanoclusters on Water-Soluble Supports," Eve S. Steigerwalt, Charles M. Lukehart, and Kevin M. Warren, American Chemical Society, 216th National Meeting, August 1998, Boston, MA.

"Rapid Synthesis of Carbon-Supported Metal Nanocrystals,"Deborah L. Boxall, William D. King, and Charles M. Lukehart, American Chemical Society, 216th National Meeting, August 1998, Boston, MA.

"From Molecules to Nanocomposites," Charles M. Lukehart, Southern Illinois University, October 1998, Carbondale, IL.

"Designed Syntheses of Binary Metal Alloy Nanocomposites Using Single-Source Molecular Precursors," Charles M. Lukehart, Seventh Annual Consortium for nanostructured Materials, October 1998, Richmond, VA.

"Designed Syntheses of Intermetallic or Alloy Binary Metal Nanocomposites Using Single-Source Molecular Precursors," C. M. Lukehart, D. L. Boxall, J. P. Carpenter, J. D. Corn, F. E. Jones III, W. D. King, and S. B. Milne, American Chemical Society, Southeast Regional Meeting, November, 1998, Research Triangle Park, NC.

"Pt-Ru and Pt-Sn/Vulcan Carbon Nanocomposites of Controlled Stoichiometry Prepared from Single-Source Molecular Precursors as DMFC Catalysts," D. L. Boxall, J. D. Corn, F. E. Jones III, W. D. King, and C. M. Lukehart, 1998 Fuel Cell Seminar, November 1998, Palm Springs, CA.

(6) List of all Participating Scientific Personnel (employed or unemployed)

(a) Angie Anderson; graduate student

(b) Debra L. Boxall; graduate student

(c) James D. Corn; graduate student

(d) Dr. Maheswaran Hariharasarma; 1/1/98 - present

(e) Frank E. Jones, III; graduate student

(f) Dr. William D. King; postdoctoral associate

(g) Krzysztof C. Kwaitkowski; graduate student

(h) Stephen B. Milne; graduate student and postdoctoral associate

(i) Joshua Moore; graduate student

(j) Eve S. Steigerwalt; graduate student

(k) Kevin M. Warren; graduate student

Degrees Awarded During Project Period:

Stephen B. Milne, Ph.D. degree in chemistry, August 1995

"Preparation of Transition Metal Phosphide, Metal, or Metal Oxide Nanocomposites"

Frank E. Jones III, M.S. degree in chemistry, May 1997

"Preparation of Mixed-Metal, Metal, or Transition Metal Phosphide Nanocomposites"

Kevin M. Warren, M.S. degree in chemistry, December 1997

"Measurement of Beta and Eta_2 for Platinum/Silica Xerogel Nanocomposites and Preparation of Gold Quantum Dots on Sodium Bicarbonate"

(7) Report of Inventions

"Polymetallic Precursors and Compositions and Methods for Making Supported Polymetallic Nanocomposites," U.S. Patent Application, Number 09/099,556 (103 pages).

(8) Bibliography

See ARO proposals for awarded projects DAAH04-95-1-0146 and DAAG55-98-1-0362 for a complete citation of related scientific literature.