Use of Sol−Gel Chemistry for the Preparation of Cyanogels as Ceramic and Alloy Precursors

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The reaction of aqueous solutions of K_2PdCl_4 and $K_3Co(CN)_6$ results in gellike polymeric materials, characterized by bridging cyanides between the central metals of the adducts. These materials tend to be rigid in nature but contain in excess of 95% water by weight. We refer to these novel transition metal based hydrogels as cyanogels. In contrast to classic inorganic hydrogels these materials are not based on an oxide network. Dehydration of the cyanogels results in amorphous xerogels which maintain the initial polymeric structure of the cyanogel. Thermal processing of gels containing palladium and cobalt centers under an inert atmosphere at temperatures between 200 and 500 °C, produces a new metastable material. Sintering between 500 and 1000 °C produces ferromagnetic alloys, while processing under oxygen in the same temperature region gives the ceramic mixed oxide material $PbCoO_2$, having the delafossite structure.

Introduction

Solution sol−gel processing has become a versatile ceramic processing technique, and basic research in this area has increased tremendously.[1−3] Classic inorganic hydrogels are obtained via polymerization of oxo species, resulting in an oxide-based network. The advantages of this processing as compared to the conventional "powder" route are that ultrahomogeneous, multicomponent systems can be obtained by mixing the molecular precursor solutions. Temperatures required for material processing can be noticeably lowered, and rheological properties of sols or gels allow the formation of fibers, films, or composites by such techniques as spinning, dip-coating, or impregnation.[1] We now report the chemistry of thermal processing of a new polymeric inorganic hydrogel,[4] made by reacting aqueous solutions of K_2PdCl_4 and $K_3Co(CN)_6$. The product polymer is characterized by bridging cyanides between the adducts metal centers. Because of the cyanide ligand framework which is central to these gels, we refer to them as cyanogels.

The increasing demand for the high-performance materials has resulted in the development of new manufacturing processes for high-temperature alloys.[5] Pd alloys are known materials,[6] normally prepared by melting metals in an arc furnace, an energy-intensive process.[7,8] These alloys have found practical applications in advanced computer storage technology as suitable recording media for magnetooptical data storage systems.[9−11] By exploitation of the sol−gel method to prepare the same materials, temperatures as low as 650 °C can be employed. In addition, the same method provides a convenient tool for the preparation of new materials. Here we report on sol−gel-derived delafossite material, Pd/Co alloys, and their unique metal sponge forms.

Experimental Section

Typically cyanogels were prepared by mixing aqueous solutions of 60 mM $K_3Co(CN)_6$ and 60 mM K_2PdCl_4 at room temperature. The formation of the spongy alloy material reported here required starting with a cyanogel prepared from 500 mM $K_3Co(CN)_6$ and 500 mM K_2PdCl_4 solutions warmed to ~80 °C to increase solubility. To prepare different molar ratios of Pd to Co in the sols, the volumes of each solution were varied. Both starting materials were obtained from either Alfa or Aldrich. Deionized water was utilized for all solutions. The gelation time was determined as the moment when the vial containing the gel could be shaken without the contents flowing. Aging of the gels, which took normally a week, was carried out at room temperature. The product after drying of the gel by evaporation at standard pressure and at a temperature close to the boiling point of the solvent is called a xerogel and was prepared by smearing the gels on filter paper and then oven drying at 95 °C to remove water. Xerogels were sintered either in a quartz tube inserted into a furnace or as a sample in a thermogravimetric (TGA) balance. In both cases, the atmosphere above the sample was purged

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with a constant flow of either argon or oxygen using a flow rate of 60 mL/min. The highly hazardous evolved gases were trapped by a series of two aqueous solutions. The bubbler contained first bleach, and the terminal bubbler contained a NaOH solution.

UV−vis spectra were recorded from a HP 8452A diode array spectrophotometer. FTIR spectra of KBr pressed pellet samples were performed in the 4000−400 cm^{-1} range on a Nicolet 730 FTIR spectrometer. Thermal analyses were recorded either on a Mettler TA-3000, a DuPont 951, or a Perkin-Elmer TGA-7. Magnetic transition temperatures were monitored using thermogravimetric analysis (TGA) in a Guoy balance configuration. Calorimetric data were obtained using a Perkin-Elmer DSC-7 instrument. About 10 mg of the xerogel was used for each analysis, performed at a heating rate of 6 °C/min. X-ray powder diffraction (XRPD) analyses were obtained on a Scintag PAD V ($\theta-2\theta$) X-ray powder diffractometer using Cu Kα radiation and a solid-state germanium−lithium detector. Samples were scanned from the quartz zero background at the rate of 1°/min. Qualitative phase analysis of the reaction products was performed using a continuous scan. Pattern indexing and the lattice parameters calculations were carried out using the program TREOR.[12]

Evolved gas analysis by mass spectrometry (EGA-MS) of thermolyzed xerogels was performed in an ion-pumped stainless steel ultrahigh-vacuum chamber equipped with INFICON IQ-200 quadropole mass spectrometer. The mass spectrometer ionizer was enclosed in a thin metal cylinder (2 in. diameter) with a coaxial entrance aperture of 0.25 in. diameter. This shield served to reduce the signal from background gas desorption. The base pressure of the system was kept below 1×10^{-9} Torr. Gasses were admitted into the vacuum chamber through a doser attached to a quartz tube with about 10 mg of sample, heated at the heating rate of 1 °C/s. The system was pumped until no signal occurred by mass spectral analysis, after each analysis set.

Inductively coupled plasma (ICP) spectroscopy was done on a Perkin-Elmer Model 6000 ICP spectrometer. Electrical resistivity of product materials was measured using a four-probe dc current method.[13,14] Conducting silver epoxy (EPO-Tek, H-32) was used to attach the back contact to a copper wire, which was then covered with nonconducting epoxy resin. Surface areas of the samples were determined from the BET isotherms using Micromeritics Flowsorb II 2300 at liquid nitrogen temperature. The samples were heated at 250 °C for 30 min, and nitrogen was used as an adsorbent.

Scanning electron micrographs (SEM) were taken from JEOL 840 (image output was Polaroid P/N 55 film). For elemental composition analysis of alloys, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed, using a Philips CM20 ST TEM/STEM operated at 200 kV and equipped with an energy-dispersive X-ray spectrometer (EDX) and a parallel detection electron energy loss spectrometer (EELS). A Philips 400 TEM/STEM microscope operated at 120 kV was used for particle size and shape determination. For the TEM experiments the samples were well powdered, dispersed in water, and then suspended on a perforated carbon film. A Guttan low-temperature sample holder cooled to liquid nitrogen temperature was used for the TEM imaging and EDX experiments.

Results and Discussion

General Observations. Mixing a 10 mL (60 mM) solution of $K_3Co(CN)_6$ with 20 mL (60 mM) of K_2PdCl_4 produces an orange sol, which in 30−40 min, at the end of the sol−gel transition, forms an elastic orange gel. The spectrophotometric method of continuous variation[15,16] (Job plots) was used to determine the molar composition of the sol. Formation of the coordination polymer (in the sol phase) is accompanied by the growth of a new electronic transition centered at 384 nm. The intensity of the at 384 nm transition as a function of mole fraction of palladium suggests a Pd/Co ratio in the sol product of either 2/1 or 3/2. The 2/1 ratio is the more likely of the two based on the results of IR spectroscopy (described later). Variations from this range of ratios increase the gelation time. Gelation time can be also increased by lowering the temperature to somewhere between 5 and 15 °C or by decreasing the concentrations of reactants. Most of the results reported here were obtained using Pd/Co = 2/1 gels and xerogels, unless specifically noted. When using 500 mM solutions of $K_3Co(CN)_6$ and K_2PdCl_4, a dark red, very hard gel was formed within a minute. It was used in the preparation of the spongy alloy material.

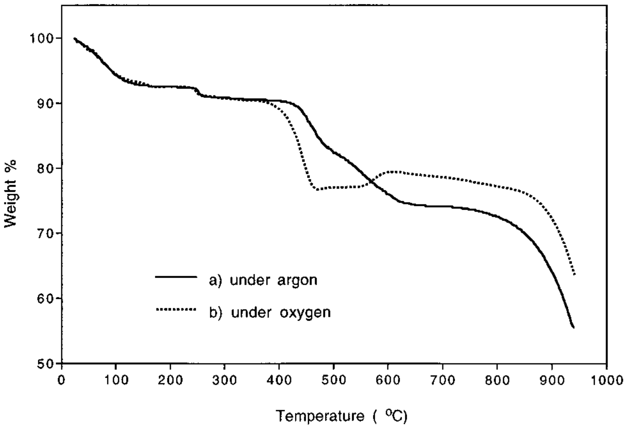

Figure 1. TG curves for 60 mM, Pd/Co = 2/1 xerogel, monitored under an (a) argon and (b) oxygen atmosphere.

Thermal Analysis. The gel is initially composed of 99% water by weight, based on thermogravimetric results, but during aging slowly loses water, shrinks in volume, and then stabilizes at ~95% water. Thermolysis of the gels were performed in two steps. During the first step, gels aged for a week were dried to xerogels in an oven at 95 °C for 6−12 h, to remove most of the water. The second step involved sintering the xerogel at elevated temperatures up to 1000 °C. The sintering process of the xerogel was followed using thermogravimetry (TG) along with derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC).

Typical TG curves of the xerogel, monitored under an argon or oxygen atmosphere, are shown in Figure 1 and DSC curves in Figure 2. Initial mass loss from 30 to 100 °C involves an endothermic reaction and is associated with removal of (~7 wt %) residual water in the xerogel.

A second mass loss occurs at 245 °C under argon. This exothermic reaction is associated with the loss of cyanide as cyanogen $(CN)_2$ from the Co metal (as discussed later), which is consistent with the published data on the thermal analysis of similar cyano complexes.[17,18] The DSC data (Figure 2) indicate that

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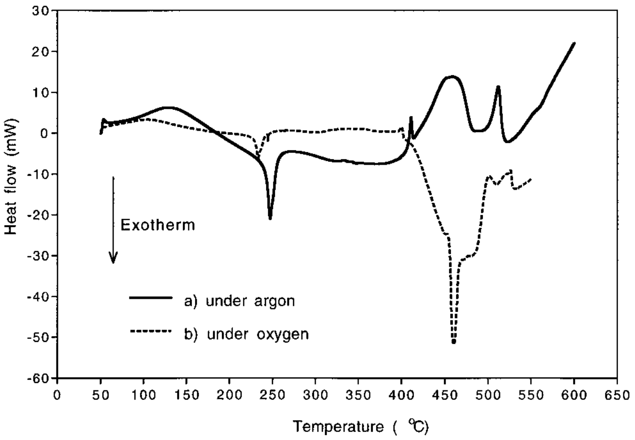

Figure 2. DSC curves for 60 mM, Pd/Co = 2/1 xerogel, monitored under an (a) argon and (b) oxygen atmosphere.

the reaction occurs over a 10 °C interval, yielding a specific heat of reaction, $\Delta H_{(CN)_2}$, of −40 J/g. Evolved gas analysis indicates that about half an equivalent of cyanogen is evolved at this point. The initial yellow color of the xerogel changes reversibly to green in this temperature interval. Addition of water changes the green powder back to yellow. If the thermolysis is carried out in the presence of oxygen, the $(CN)_2$ evolution reaction is found to occur at a slightly lower temperature (240 °C), with $\Delta H_{(CN)_2} = -62$ J/g.

The third notable mass loss under an argon atmosphere starts at 410 °C. Decomposition proceeds until around 650 °C, where the mass loss reaches a plateau. As will be described in the EGA-MS experiment, this endothermic reaction with $\Delta H = 370$ J/g is associated with the coevolution of cyanogen and hydrogen cyanide. During that mass loss interval, the color of the powder irreversibly changes to deep blue and finally black. We speculate, on the basis of the shape of DTG and DSC curves in this temperature region, that the cyano ligands are released stepwise, depending on their stereochemistry.

No change of mass in the 650−700 °C region was detected under argon, but a rapid mass loss is seen again at 700−1000 °C, which we associate with KCl sublimation,[19] an endothermic reaction.

In contrast to thermolysis under argon, the presence of oxygen introduces a number of mass changes in the 380−700 °C interval. A stoichiometric mixture of oxygen and cyanogen burns, producing a ~5050 K flame.[20] Thus, this reaction is exceedingly exothermic. This explains the extreme exothermicity ($\Delta H = -1790$ J/g) of the third mass loss in the 380−500 °C interval (see Figures 1b and 2b) when sintering is carried out under an oxygen atmosphere. We assign this reaction to the evolution of cyanogen, on the basis of the EGA-MS experiment, shown in Figure 3. Additionally, sintering of ~10 g of xerogel in a quartz tube was found to damage the quartz glass, consistent with a highly exothermic reaction.

In the 520−700 °C temperature interval a mass increase is observed only when the xerogel sample is under an oxygen atmosphere. An endothermic reaction which we assign to oxygen uptake is observed by DSC analysis with $\Delta H = 2.4$ J/g and results in formation of the mixed oxide $PdCoO_2$ with delafossite structure,[21] Pd metal, PdO, and Co_3O_4, as described later under XRPD results. The ratio of oxides being produced depends on the initial Pd/Co ratio in the gels and whether the xerogel was prepared from fresh or aged gel. At ~700 °C oxygen uptake starts to compete with further decomposition of the sample. Above this temperature the endothermic sublimation of KCl is observed, similar to the reaction under argon.

TG analysis was carried out on xerogels having three different Pd/Co ratios from room temperature to 1000 °C. Increasing the mole ratio of hexacyanocobaltate (from 0.33, 0.50 to 0.67) in the starting gel, caused the starting point of the second and third mass loss to consistently shift ~40−60 °C to higher temperatures. This finding suggests that the highest ratio of the

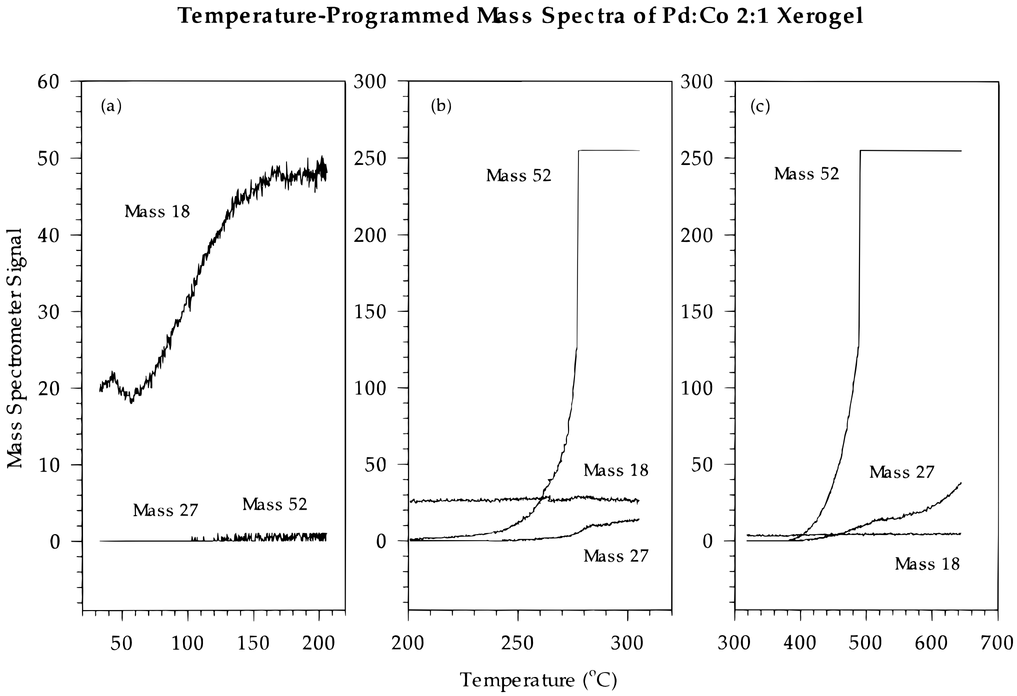

Figure 3. EGA-MS analysis of a 60 mM, Pd/Co = 2/1 xerogel, obtained in three steps following the main three mass losses detected in the thermogravimetric curves. Step one was run from 25 to 200 °C, step two at 200 to 305 °C, and step three at 305 to 650 °C.

bridging cyanides over terminal ones is present in the gels with Pd/Co ratio of 2/1. Bridged cyanides have lower binding energy to cobalt than terminal cyanides, making them less stable toward thermal decomposition. (See discussion on FTIR spectroscopy which follows.) Therefore, cyanogen evolution is shifted to lower temperatures as the ratio of bridged to terminal cyanides increases. If one compares the thermal decomposition of Pd/Co xerogels with that of $K_3Co(CN)_6$[18,22] (which obviously has only terminal cyanide ligands), it can be seen that temperatures of ≥500 °C are necessary to observe cyanide loss. Further, unlike the thermal decomposition of the Pd/Co cyanogel, the thermolysis of $K_3Co(CN)_6$ is quite complex, leading to a variety of carbon-based products and not the clean formation of cyanogen. The starting point of oxygen uptake in Pd/Co xerogels in the course of sintering is also consistently shifted toward lower temperature with increasing ratio of the bridging over terminal cyanides, indicating that cyanide ligands must be evolved prior to reaction with oxygen to form oxide products.

Evolved Gas Analysis by Mass Spectrometry. EGA-MS analysis of a Pd/Co = 2/1 xerogel was run in three steps as shown in Figure 3, basically following the main three mass losses detected in the thermogravimetric curves. In the first step, which was run from 25 to 200 °C, only mass 18 was detected, corresponding to the evolution of water. A large signal for mass 52 (cyanogen) started to appear in step two at ~230 °C. This signal saturated the MS detector. A trace amount of hydrogen cyanide with mass 27 was also observed in step two starting at 280 °C. Evolution of cyanogen continued in step three at ~390−650 °C, in agreement with the starting temperature of the third large mass loss observed by TG. A small amount of HCN continued to form through this temperature range. A similar experiment was run using $K_3Co(CN)_6$, and as expected from the TG curve, no decomposition and hence cyanogen formation was detected up to 500 °C.

FTIR Spectroscopy. Infrared spectroscopy of the hydrogel is hindered by the fact that the cyanide stretching vibrations in 2000−2200 cm^{-1} region and below 700 cm^{-1} are overlapped by the water vibrations. However, this problem can be circumvented by carrying out FTIR analysis of xerogels.

The FTIR spectrum of $K_3Co(CN)_6$ has one sharp stretching vibration ν(CN) at 2128 cm^{-1}, and two in the low-frequency region, a stretching vibration, ν(CoC), at 565 cm^{-1} and a bending vibration, δ(CoCN), at 417 cm^{-1}, as assigned previously.[23] The FTIR spectra of Pd/Co xerogels show a shift of the cyanide stretching vibrations in the high-wavenumber region, to higher frequency, at 2144 and 2196 cm^{-1} (see Figure 4a). The 2144 cm^{-1} band corresponds to the terminal stretching vibrations, ν(CN), of the cyanides on cobalt, while the 2196 cm^{-1} stretch corresponds to bridging cyanides (Co−CN−Pd), by analogy to similarly bridged species.[23−25] The two large peaks near 3500 and 1600 cm^{-1} are due to the residual water in the xerogel. In the low-wavenumber region, there is a major peak at 501 cm^{-1} (see Figure 4a) with a shoulder at 480 cm^{-1} which we assign to the ν(CoC) stretching vibrations and a broad peak at 570 cm^{-1} assigned to a Co−CN−Pd bending mode.[23,26,27] Changing the ratio of Pd/Co in the gels reflects significantly on the ratio of bridging to terminal cyanide stretchings, being the highest for 2/1 xerogels.

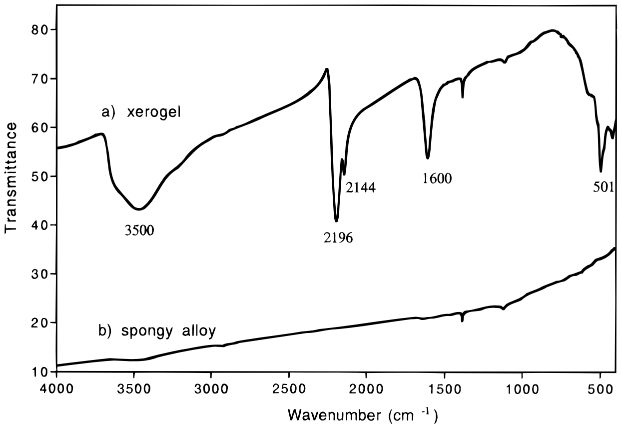

Figure 4. Transmittance FTIR spectra of 60 mM, Pd/Co = 2/1 (a) xerogel sample and (b) the same sample sintered at 1000 °C under argon.

Samples which were taken along the main TG inflection points of Pd/Co = 2/1 run under oxygen were analyzed by FTIR as shown in Figures 5 and 6. Heating of the gel to ~200 °C did not cause significant change in either the low- or high-wavenumber FTIR spectral regions (Figures 5a and 6a). At 240 °C the second notable mass loss is observed in the TG data. At this temperature some of the cyanide bridges are observed to have decomposed (Figures 5b and 6b), causing evolution of half an equivalent of cyanogen. This process is also associated with the formation of different decomposition products. It is possible that the number of coordinated cyanide ligands on Co is decreasing, seen by the shift of the terminal cyanide stretching vibrations, ν(CN) to higher frequency[23] as seen by the three peaks at 2236, 2221, and 2176 cm^{-1} and in the low-frequency region decrease of the ν(CoC) stretching vibrations to 458 cm^{-1}. After the second inflection point (280 °C) a very pronounced peak at 2194 cm^{-1} is seen in the high-frequency region (Figure 5c) along with the further shift of two peaks in the low-frequency region to 534 and 451 cm^{-1} which we tentatively ascribe to the stretching vibration and bending modes of cyanide ligands[23,28,29] in $Co(CN)_n$ ($n < 6$). It is also possible that these transitions are due to the to formation of $KPdCo(CN)_6$ compounds, or to formation of $Pd(CN)_2$ formed by the "flipping" of the cyanide bridges[30−33] to form Co−NC−Pd bridges.

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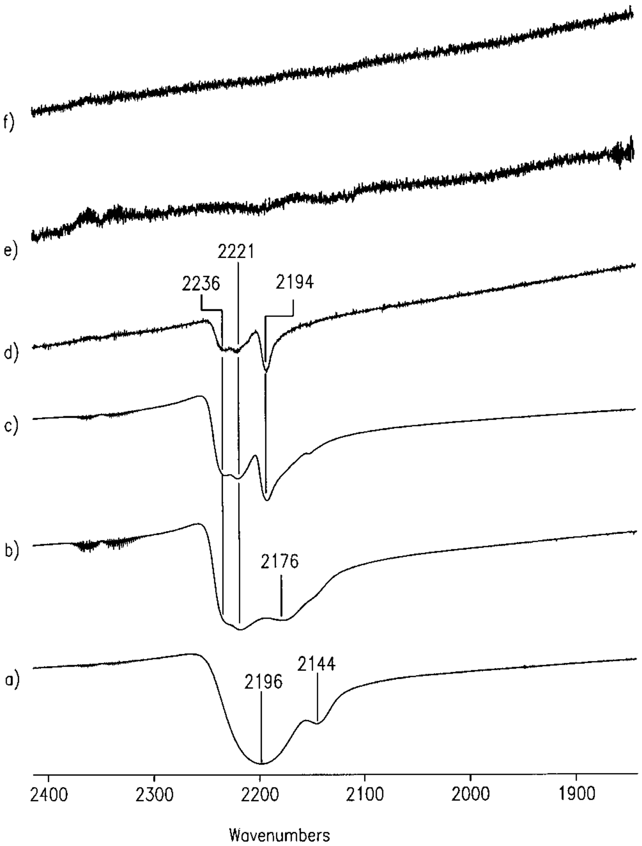

Figure 5. High-frequency transmittance FTIR spectra of 60 mM, Pd/Co = 2/1 xerogel samples, which were taken along the main TG inflection points, run under oxygen, at (a) 150, (b) 240, (c) 280, (d) 420, (e) 650, and (f) 795 °C.

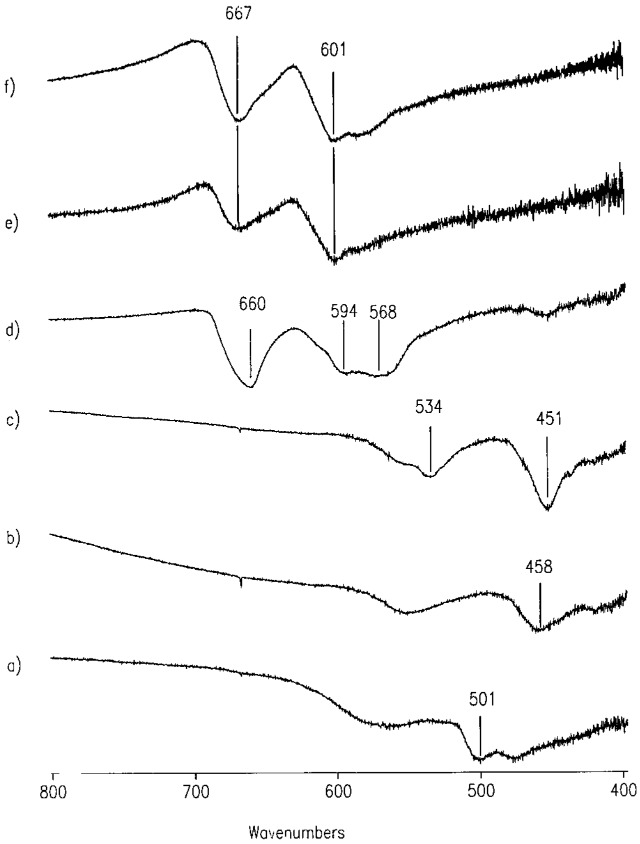

Figure 6. Low-frequency transmittance FTIR spectra of 60 mM, Pd/Co = 2/1 xerogel samples, which were taken along the main TG inflection points, run under oxygen, at (a) 150, (b) 240, (c) 280, (d) 420, (e) 650, and (f) 795 °C.

Passing through the third mass loss under an oxygen atmosphere at 500 °C (and 650 °C under an argon atmosphere) removes all high-wavenumber vibrations (Figures 4b and 5e,f). Mixed oxides start to form under an oxygen atmosphere, simultaneously with decomposition of cyanides (Figure 5d), generating Pd−O and Co−O stretching vibrations[34−36] at 660, 594, and 568 cm^{-1} (see Figure 6d).

Under an argon atmosphere the thermal profile up to ~400−500 °C is similar to that observed under an oxygen atmosphere. Above 650 °C no IR peaks are observed in either the low- or high-frequency regions, excluding the formation of carbides a typical thermal decomposition product, associated with the thermolysis of terminal cyanometalates.[22,37]

TEM/STEM/EELS/EDX and SEM Experiments. The TEM method, operating in a diffraction mode, showed that the Pd/Co = 2/1 xerogel initially had an amorphous nature, but after a few seconds under the electron beam, this material underwent a phase transition, becoming crystalline. The powder diffraction pattern shown in Figure 7 indicated that the material was polycrystalline with a fcc lattice structure. The electron diffraction image obtained is similar to the X-ray scattering of the thermolyzed product and is assessed to be due to thermolysis of the TEM sample by the electron beam. The EDS analysis of the black powder obtained by thermolyzing the less concentrated gel (Pd/

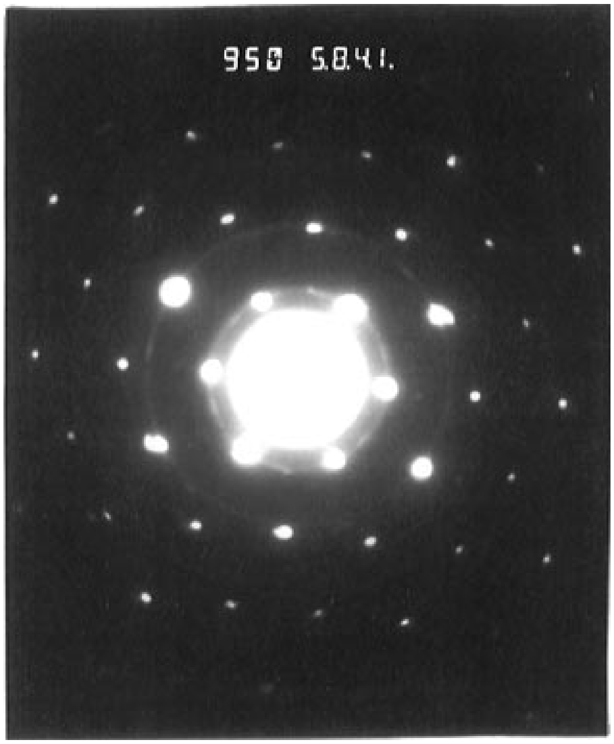

Figure 7. TEM picture of 60 mM, Pd/Co = 2/1 xerogel after a few seconds under an electron beam. The ring diffraction pattern indicate that initially amorphous material became polycrystalline with a fcc lattice structure.

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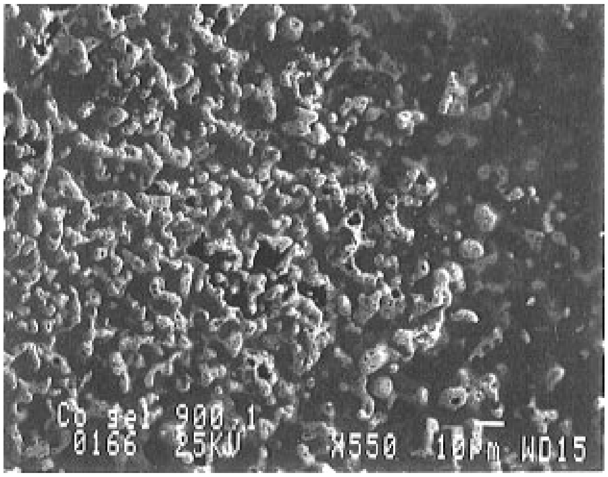

Figure 8. STEM picture of the spongy metallic alloy (prepared from 500 mM solutions of $K_3Co(CN)_6$ and K_2PdCl_4 with the ratio of Pd/Co = 2/1, after sintering at 1000 °C under an argon atmosphere), showing its porous nature.

Co = 2/1, 60 mM) shows that the alloy has a very homogeneous structure and a Pd/Co ratio very close to the initial ratio (1.85/1); similarly, a nonstoichiometric Pd/Co 1/1 xerogel produced a product having a Pd/Co ratio of 0.85/1. The spongy alloy obtained from the 500 mM, Pd/Co = 2/1 gel after sintering for 10 h at 1000 °C, showed a ratio of Pd/Co = 2.5/1. The analyses also showed trace amounts of potassium and chloride in both materials. The scanning electron micrograph of the black powder shows the crystalline material with grains size ~200 Å, while the micrograph of the spongy metallic alloy (Figure 8) shows the porous nature of that material.

X-ray Powder Diffraction and Physical Characterization. XRPD analysis of xerogels after being thermolyzed up to 400 °C under argon atmosphere, shows only a pattern for KCl, along with an amorphous component. A pure palladium diffraction pattern starts to grow in at 413 °C; above 600 °C the diffraction pattern is indicative of a Pd/Co alloy having the fcc structure. The alloy diffraction pattern is unchanged up to 1000 °C (the highest temperature investigated). At 1000 °C practically no KCl is observed by XRPD, which confirms that the significant mass loss at temperatures of 700−1000 °C (by TG) is due to KCl loss.

When a bulk sample of the Pd/Co 2/1 xerogel prepared from the concentrated (500 mM) gel was sintered at 1000 °C for 10 h under argon, a black metallic substance resulted which behaved like a sponge after being washed in water. Small amounts of KCl and Co were detected with inductively coupled plasma analysis (ICP) in the water after washing. One gram of the metallic product material absorbed 1.35 g of water, which could be partially removed by squeezing the material by hand or completely removed by heating to 150 °C for about 3 h. Mechanical removal of the water (by squeezing) and "rehydration" was found to be a reversible (and reproducible) process. Black powder rather than spongy alloy was obtained after sintering under argon if the cyanogel was prepared from 60 mM solutions, or the ratio of Pd/Co was different from 2/1, or if the xerogel was washed with deionized water prior to sintering, until no Cl^- ions could be detected in rinsing water. An experiment in which an excess of KCl was added to the concentrated washed gel, showed that the presence of alkali-metal halides is necessary for the formation of metallic sponge.

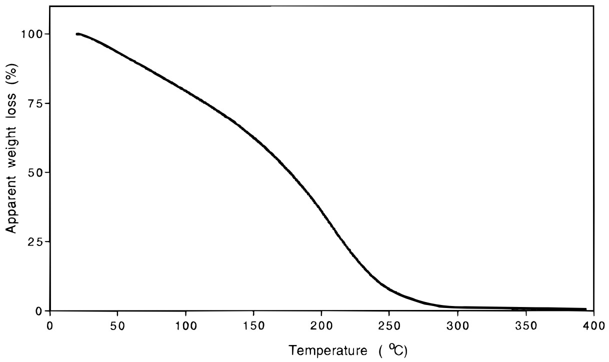

Figure 9. Determination of the magnetic Curie point temperature for the spongy metallic alloy (prepared from 500 mM solutions of $K_3Co(CN)_6$ and K_2PdCl_4 with the ratio of Pd/Co = 2/1, after sintering at 1000 °C under an argon atmosphere). The data were obtained by noting the apparent weight of a sample of spongy alloy in a magnetic field gradient (15 G) as a function of sample temperature. Since the magnetic susceptibility of a sample is directly proportional to the apparent weight loss, the Curie point is defined by the temperature of the inflection point in the graph.

Table 1. Comparison of the XRPD Pattern Result for the Sponge Alloy (Prepared from 500 mM $K_3Co(CN)_6$ and 500 mM K_2PdCl_4 Solutions with the Ratio Pd/Co = 2/1, after Sintering at 1000 °C for 10 h under an Argon Atmosphere) with the Patterns for Palladium and Cobalt from the JCPDS-ICDD[40] Database)

h k l	palladium (d)/(I/I_{max}) JCPDS-ICDD 5-681	cobalt (d)/(I/I_{max}) JCPDS-ICDD 15-806	alloy (d)/(I/I_{max}) observed
1 1 1	2.2459/100	2.0467/100	2.21129/100
2 0 0	1.9449/42	1.7723/40	1.9149/29
2 2 0	1.3759/25	1.2532/25	1.35409/14
3 1 1	1.1729/24	1.0688/30	1.15473/12
2 2 2	1.1231/8	1.0233/12	1.10527/7
3 3 1	0.923/13		0.87872/6
4 2 0	0.8696/11		0.85607/6

Table 2. XRPD Result of the Sample (Prepared from the Gel of 60 mM $K_3Co(CN)_6$ and 60 mM K_2PdCl_4 with Pd/Co Ratio 2/1) Thermolyzed at 400 °C under Oxygen Atmosphere, Which Exhibits a Tetragonal Symmetry[a]

d observed	2θ observed	intensity I/I_{max} observed	2θ calculated	*h k l* predicted
2.8419	31.454	100	31.456	2 1 0
2.4426	36.765	8	36.776	1 0 2
2.0094	45.083	49	45.082	3 1 0
1.6414	55.978	12	55.974	1 1 3
1.2725	74.504	8		

[a] Calculated values for the tetragonal structure: $a = b = 6.354$, $c = 5.290$, $\alpha = \beta = \gamma = 90°$, unit cell volume is 213.6 Å^3. The fifth observed value was not used in the calculation.

The X-ray powder diffraction data (Table 1) for the sponge alloy indicates a fcc lattice structure as is observed for both pure Pd and pure Co crystals. The lattice parameter is found to be 3.8296 Å. The powdered form of the Pd/Co alloy yields a = 3.8254 Å, which is close to a linear extrapolation between the lattice constants of both metals (3.8898 Å for palladium and 3.5447 Å for cobalt). Our XRPD results are in very good agreement with reported data[38] for the alloys obtained by melting different ratios of the pure metals under argon at 1800 °C.

As expected for Pd/Co alloys[6,38] we find our alloys (both sponge and powder) to be ferromagnetic. A Curie temperature (ferromagnetic to paramagnetic transition) of 300 °C was determined for Pd/Co = 2.5/1 spongy alloy,

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Table 3. Comparison of the XRPD Pattern Result for the Sponge Alloy (Prepared from 500 mM $K_3Co(CN)_6$ and K_2PdCl_4 Solutions with the Ratio Pd/Co = 2/1, after Sintering at 1000 °C under an Oxygen Atmosphere) with the JCPDS-ICDD[40] Files for $PdCoO_2$ 27-1324, PdO 41-1107, Co_3O_4 42-1467, and Pd 5-681

d observed	I/I_{max} observed	assigned products	$PdCoO_2$ $(d)/(I/I_{max})$	PdO $(d)/(I/I_{max})$	Co_3O_4 $(d)/(I/I_{max})$	Pd $(d)/(I/I_{max})$
5.91	5	$PdCoO_2$	5.91/45	3.046/3	4.667/19	2.2459/100
4.62	2	Co_3O_4	2.956/90	2.669/22	2.858/34	1.9449/42
2.95	30	$PdCoO_2$	2.427/80	2.647/100	2.437/100	1.3759/25
2.86	5	Co_3O_4	2.362/100	2.153/14	2.334/9	1.1729/24
2.66	2	PdO	2.145/85	2.007/1	2.021/19	1.1231/8
2.63	10	PdO	2.017/15	1.6762/20	1.6501/8	0.9722/3
2.44	10	Co_3O_4	1.971/50	1.5365/15	1.5557/29	0.923/13
2.43	80	$PdCoO_2$	1.7616/30	1.5228/11	1.4290/34	0.8696/11
2.36	100	$PdCoO_2$	1.6445/85	1.3347/6	1.3664/2	
2.24	10	Pd	1.4788/35	1.3227/15	1.2782/2	
2.14	80	$PdCoO_2$	1.4373/70	1.3197/13	1.2328/7	
2.01	5	$PdCoO_2$	1.4149/65	1.1344/3	1.2187/4	
1.96	50	$PdCoO_2$	1.3762/15		1.1668/2	
1.944	5	Pd	1.3474/15		1.1319/1	
1.75	20	$PdCoO_2$	1.2762/65		1.0802/3	
1.68	2	PdO			1.0524/9	
1.64	80	$PdCoO_2$				
1.543	5	Co_3O_4				
1.47	30	$PdCoO_2$				
1.44	20	$PdCoO_2$				
1.43	5	Co_3O_4				
1.42	60	$PdCoO_2$				
1.378	2	Pd				
1.368	10	$PdCoO_2$				
1.345	10	$PdCoO_2$				
1.271	60	$PdCoO_2$				
1.175	2	Pd				

as shown in Figure 9, which is similar to the value reported for the classically synthesized alloy of the same composition.[6]

Nitrogen BET isotherms were used to measure the surface area of the alloy products found by thermolysis under argon. The black powder was found to have a surface area of 35.46 m^2/g, while the metallic sponge yielded a 5.16 m^2/g surface area.

The measured specific electrical resistivity of the spongy alloy when pressed into a thin pellet was 4.99×10^{-4} Ω cm, which is only an order of magnitude larger than the reported value of $(2-4) \times 10^{-5}$ Ω cm for the Pd/Co alloys prepared in an arc furnace at 1150 °C from the pure metals.[8,39] The specific resistivity of the swollen metallic sponge was an order of magnitude larger (5.14×10^{-3} Ω cm).

After thermolysis of the samples under an oxygen atmosphere, XRPD data showed no other crystalline phase other than KCl until 400 °C, when a new phase was detected. The observed reflections are reported in Table 2, and since the required structure was not found among available JCPDS-ICDD[40] files, a possible tetragonal cell was calculated. The unit cell volume is calculated to be 213.60 $Å^3$. A four-line pattern is calculated and found with a fifth low-intensity line ($2\Theta = 74.504°$) unidentified.

Sintering of xerogels at 1000 °C under an oxygen atmosphere produced three different oxides, $PdCoO_2$, PdO, Co_3O_4, and pure Pd, depending on the initial Pd/Co ratios in the aged xerogels. The gel with a Pd/Co ratio of 2/1 (60 mM) which had been aged for a week at the room temperature produced a ceramic material of the form $PdCoO_2$ with a delafossite-type structure[21,41,42] based on the XRPD data presented in Table 3. A small impurity (~10%) of three other products is also observed. Delafossite material was not obtained from fresh gels, which suggests that further cross-linking of the polymer network takes place after the sol−gel transition point.[2]

Conclusions

The thermolysis of octahedral transition-metal cyanometalate complexes (including hexacyanocobaltate) typically leads to the formation of mixed products containing metal carbides, formed by cleavage of the cyanide C−N bond.[22,37] In contrast to this behavior, the thermal chemistry of the cobalt−palladium cyanogel involves clean removal of the intact cyanide ligands as cyanogen. This process is observed both for bridging cyanides which form the coordination polymeric network and for terminal cyanide ligands. Since cyanogen is formed by the oxidation of cyanide, formation of the cyanogel network apparently activates a redox pathway for ligand loss. Consistent with this conclusion is the observation of reduced metal products when the thermolysis is carried out in the absence of oxygen. We have previously noted, on the basis of electrochemical measurements that formation of bridging cyanides shifts the redox potential of a cyanometalate complex positive by 200−300 mV/bridging cyanide, when compared to a complex having only terminal cyanides.[4,43−45] Thus, formation of the cyanogel polymer structure is expected to make the incorporated metallic species easier to reduce. Since the cobalt−palladium cyanogel does not exhibit a reversible electrochemical response, it is not

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possible to directly examine this system's thermodynamic redox behavior. If it is assumed to behave in a manner similar to other group 10/group 8 bridging cyanide systems we have studied, then the expected shift in the thermodynamic ease of reduction could account for the introduction of the observed ligand loss redox pathway.

Unlike classical thermal sol–gel processing of inorganic alkoxy polymers, the chemistry of cyanogels shows a high degree of synthetic versatility allowing for a variety of well defined solid-state products depending on the chemical composition of the processing environment. This concept is demonstrated using the cobalt/palladium cyanogel in the present study. Thermolysis of this material in the presence of oxygen provides a new low-temperature route to the generation of $PdCoO_2$ ceramics. Alternately, thermolysis in an anaerobic environment leads to the formation of ferromagnetic palladium–cobalt alloys having unique morphologies and physical properties with respect to bulk interactions with water. Preliminary evidence from our laboratory suggests that cyanogels in general are amenable to this type of processing to generate a diversity of products. Thus, cyanogel chemistry opens up the possibility of using sol–gel processing to access a wide variety of solid-state materials without the limitation of current processing that they be oxide based.

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