

HIGH-SURFACE-AREA, DUAL-FUNCTION OXYGEN ELECTROCATALYSTS
FOR SPACE POWER APPLICATIONS

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We investigated the processes of hydration/dehydration and carbonation/decarbonation as an approach to provide higher surface area mixed metal oxides that are more active electrochemically. These materials are candidates for use as electrocatalysts and electrocatalyst supports for alkaline electrolyzers and fuel cells. For the case of the perovskite, LaCoO_3 we achieved higher surface areas with no change in structure and a more active oxygen electrocatalyst.

INTRODUCTION

An energy storage system to provide energy for the dark side of orbit is required for the space station. One energy storage system concept that has received attention is the dedicated alkaline regenerative fuel cell storage system (ref. 1). This system is based on solar array, alkaline fuel cell, and alkaline water electrolyzer component technologies. The energy storage system operates on a 90-minute cycle, alternately going through dark and light side orbit environments. During the light side of the orbit, the solar array provides electrical power to the satellite module plus excess electrical power used to electrolyze water to produce hydrogen and oxygen. During the dark side of the orbit, the hydrogen and oxygen are reacted in the fuel cell to provide electrical power to the satellite module plus water which is stored for use by the electrolyzer during the light side of the orbit.

An alternative approach is the integrated alkaline regenerative fuel cell storage system (ref. 1). In this system a single electrochemical module operates in both the fuel cell and water electrolysis modes and a substantial reduction in the weight and volume of the regenerative energy storage system is achieved. However, the requirement that the hydrogen and oxygen electrodes operate in the dual function (i.e., reactant consuming, generating) mode presents a materials stability problem, particularly at the oxygen electrode.

During the past several years, numerous workers have investigated mixed metal oxides of the perovskite, spinel, and pyrochlore structures for electrochemical applications. Mixed metal oxides reportedly possess catalytic activity for both oxygen reduction and evolution in alkaline media. Additionally, these materials are attractive as support materials for the gold fuel cell catalysts. Consequently, NASA is interested in mixed metal oxides as: 1) oxygen evolution and/or reduction catalysts for the dedicated regenerative fuel cell/electrolyzer, 2) dual function oxygen electrocatalysts for the integrated regenerative fuel cells, and 3) an electrocatalyst support for high temperature and pressure alkaline fuel cells. One important problem with the mixed metal oxide materials is their relatively low surface area.

The objective of our initial research effort was the demonstration of a new technique for enhancing the surface areas of conventionally prepared mixed metal oxide catalyst materials. We accomplished this surface area enhancement using a pressure hydration/dehydration or carbonation/decarbonation technique. In this approach, we hydrated or carbonated the oxide sample at temperatures up to 400°C and pressures up to 5000 psi in a stainless steel reactor. This step was followed by dehydration or decarbonation of the oxide sample in a furnace with flowing nitrogen at 400°C. We characterized the results of this process primarily by measuring the surface areas before and after our process using the BET technique. We studied sixteen mixed metal oxide systems using forty-three different process variables and obtained surface area enhancements greater than a factor of two in eleven of these cases. In one case we observed a surface area enhancement of twenty times. For one mixed metal oxide, LaCoO_3 , we studied the degree of surface area enhancement as a function of the hydration conditions and obtained larger surface areas at lower hydration temperatures.

We characterized the crystal structure of the mixed metal oxide before and after surface area enhancement using Debye-Scherrer, and in two cases diffractometer, x-ray diffraction. In the case of LaCoO_3 , a potential oxygen electrocatalyst, we observed a surface area enhancement of nearly seven times and no change in peak positions from the x-ray diffraction analysis, indicating that the high surface area material had the same crystal structure as the initial catalyst. In the case of SrZrO_3 we obtained increased surface area, but the crystal structure was not retained in a pure form. Using the rotating disc electrode (RDE) technique, we verified increased electrochemical activity for the enhanced surface area LaCoO_3 relative to the as received LaCoO_3 .

Approach to Activity Enhancement

In selecting a catalyst to be electrochemically dual-functional, we are likely to be forced to choose a material with limited specific activity for one reaction in order to optimize overall performances. We have shown in this work that we can achieve increased catalyst activity by increasing the surface area of the catalyst material. Our approach for increasing surface areas has been successfully used for lime type SO_2 sorbent materials. To our knowledge, no similar approach has been used for preparation of any catalyst materials. We have achieved enhancements in surface areas of a variety of mixed metal oxide electrocatalysts using pressure hydration (or carbonation) followed by dehydration (or decarbonation).

The hydration and dehydration processes for one of our successfully expanded catalysts are represented by the reactions:



Similar carbonation and decarbonation processes of a successful material are



We have no way of knowing the correct form or stoichiometry of the hydrated or carbonated materials, for instance whether they are mixed or separate metal hydroxides or

carbonates. Based on our experience with lime type sorbent materials and the catalytic materials studied in this program we expect processes of these types to produce increased surface area materials for any substances that form stable hydroxides or carbonates at achievable conditions. For successful application as catalysts we also require the expanded surface area materials to have the same crystal structure as the low surface area electrocatalysts.

We can predict which mixed metal oxide systems will react with water or carbon dioxide and what conditions are appropriate for the reaction if we have thermochemical data for the mixed metal oxides and hydroxides or carbonates of interest. However, these thermochemical data are available for only a few of the many mixed metal oxides studied as electrocatalysts (ref. 2).

High Surface Area Mixed Metal Oxide Preparation

The surface area enhancement of the mixed metal oxides involved the pressure hydration or carbonation procedure described above. We purchased the mixed metal oxides to be investigated from ChemMaterials Ltd. and Alpha Products Division of Morton Thiokol. One mixed metal pyrochlore, $\text{Pb}_2\text{Ru}_2\text{O}_7$, was prepared as described in the patent literature (ref. 3).

We conducted the pressure hydration or carbonation experiments in a stainless steel reactor manufactured by Parr Instruments Inc. (Model No. 4740). The reactor volume is 71 ml and the maximum allowable pressure is 8500 psi at 350°C. In most experiments we added approximately 0.5 grams of the mixed metal oxide to the reactor and 50 ml of distilled water for the hydration experiment and 900 psi of CO_2 for the carbonation experiment, respectively. The reactor was then heated to temperature (typically 400°C) and held overnight. The reactor was then cooled to room temperature before the reactor was opened to the ambient atmosphere. We also hydrated some samples at ambient conditions. The sample was collected and dried prior to the dehydration or decarbonation step. The dehydration was usually conducted in flowing nitrogen gas at 400°C.

Characterization

We characterized the specific surface areas of the mixed metal oxides using a Micromeritics BET surface area analyzer. The initial surface areas of the mixed metal oxides were determined as received or as prepared. We also characterized the surface areas of the samples in the hydrated or carbonated form and in the dehydrated or decarbonated form.

We characterized the crystal structures of the mixed metal oxides before and after surface area enhancement using Debye-Scherrer powder x-ray diffraction. Two samples were characterized using a powder x-ray diffractometer. The Debye-Scherrer x-ray diffraction analyses were conducted at Eastern Analytical Laboratories and the diffractometer analyses were conducted at NASA Lewis Research Center.

Rotating Electrode Evaluation

When evaluating the electrochemical activity of new or novel oxygen electrocatalyst materials, many researchers prepare gas diffusion electrodes and conduct half cell experiments. One problem with this approach is that the procedure used to prepare gas diffusion electrodes for state-of-the-art electrocatalysts (e.g., unsupported gold) may not result in an optimum electrode structure for the novel electrocatalyst

material. Consequently, the polarization data would contain gas diffusion and reactant transport losses which would mask the desired kinetic polarization behavior. To avoid these problems with gas diffusion electrode preparation, we decided to evaluate the novel electrocatalyst powders using the rotating electrode technique. In the rotating disc electrode (RDE) technique, mass transport corrected kinetic and mechanistic information for the oxygen reduction may be obtained.

This technique is elucidated in a now classic compilation of earlier work (ref. 4) in which the mathematics of fluid dynamics at submerged rotating surfaces was combined with expressions for electrolysis kinetics at electrodes of various geometries. One geometry considered was the disc electrode. The electrode material is mounted on the end as a disc and surrounded by an inert shroud and is rotated while slightly submerged in the electrolyte. By fixing the rotation rate, the transport of reacting species to the electrode surface is constant. The exact relation between the diffusion layer thickness, δ , and electrode rotation, ω , has been derived:

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad , \quad (3)$$

where ω is the electrode rotation rate (rev/min), ν is the kinematic viscosity, and D is the diffusion coefficient.

Combining equation (3) with Faraday's and Fick's laws, the expression for the limiting disc current is:

$$i_l = 0.62 n F A D^{2/3} \nu^{-1/6} \omega^{1/2} C_b \quad m \quad (4)$$

where F is Faraday's constant, A is the electrode area, and C_b is the bulk reactant concentration. This equation is known as the Levich equation. Good agreement between limiting currents determined experimentally for species with known diffusion coefficients and that predicted by the Levich equation have been reported (ref. 5).

The rotating electrode experiments were conducted in an all Teflon cell using a Pine Instruments Co. Analytical Rotator and a Pine Instruments Bipotentiostat. The data were acquired using an IBM PC with 512 kB of memory and an interface board manufactured by Data Translation Inc. The oxygen reduction experiments were conducted in low concentration NaOH which was saturated with bubbling oxygen gas (99.99 percent purity). The potential was scanned from 1.0 to 0.4V versus RHE at a scan rate of 10 mV/s. The disc current and disc potential data were acquired at a rate of ten points per second or 600 points of data per rotation rate. The rotation rates used were 400 to 4900 rpm. We conducted initial RRDE experiments using smooth platinum in order to verify our technique with those reported in the literature. Several programs were written in Basic to conduct the rotating electrode analysis.

In order to evaluate the electrocatalytic activity of the mixed metal oxide powders, we modified a demountable ring-disc electrode assembly manufactured by Pine Instruments Co. and shown in figure 1. The disc electrode stem was modified to contain a 0.35 mm cavity as shown in figure 2. We applied the electrocatalyst powder to the cavity using Teflon as a binder (ref. 6). After several attempts at preparing the electrocatalyst and binder for the rotating electrode studies, the following procedure was found to be optimum. One hundred milligrams of the electrocatalyst powder was blended with 25 ml of distilled water and enough Teflon (DuPont TFE 30B) to make 20 percent Teflon by weight. The material was mixed to form a suspension and then

vacuum filtered onto a 10 μ Millipore Teflon substrate. The filtered material was allowed to air dry overnight and then sintered at 250°C for fifteen minutes. The sintering process resulted in a material with a rubbery consistency. This material was then spread into the disc cavity with a spatula and smoothed using a razor blade. The electrode was then washed in the electrolyte to insure that any surfactant from the Teflon dispersion was removed prior to beginning the rotating electrode experiment.

Specific Surface Area Characterization

The BET specific surface areas of the mixed metal oxides obtained for study in this program are given in Table 1 along with the surface areas achieved by our processing. The highest surface area we measured for materials as received is approximately 30 m²/g for the lead ruthenium pyrochlore. Most of the measured initial surface areas were 1 to 4 m²/g. The two lanthanum strontium manganates exhibited surface areas of 7 to 10 m²/g. These commercially obtained samples were reportedly prepared by the freeze drying of a stoichiometric mixture of the nitrates. Literature sources have reported higher surface areas (typically 15 m²/g) for mixed metal oxides prepared by this technique. Apparently there is a considerable discrepancy between what is possible in terms of surface area with freeze drying and what is reported.

Surface area data for the mixed metal oxides after dehydration and decarbonation are also presented in Table 1. In general hydration was more successful than carbonation. In only the case of SrZrO₃ did carbonation alone enhance the surface area of the mixed metal oxide. In two other cases carbonation as well as hydration resulted in surface area enhancement. For the SrZrO₃ mixed metal oxide the thermodynamic calculations indicated a favorable free energy of carbonation and a substantial surface area increase from 3.91 to 50.6 m²/g was indeed observed. Favorable free energies of reaction were also calculated for hydration and carbonation of MgTiO₃ and for carbonation of SrTiO₃. The hydration attempt was successful for these substances but the carbonations did not result in surface area enhancement.

We studied the effect of hydration temperature on LaCoO₃. We choose this mixed metal oxide because of the moderate degree of success of the initial hydration attempt (i.e., approximately three times surface area enhancement). The initial hydration attempt was at a temperature of 300°C. We also conducted hydrations at 400 and 200°C. The surface area data are presented in figures 3 and 4 as functions of hydration pressure and hydration temperature. For the 400°C hydration, the surface area was increased to only 3.8 m²/g (from 2.6 m²/g) while in the case of the 200°C hydration the surface area increased to 18.1 m²/g. Although the water pressure is decreasing as the reaction temperature is decreasing, we conclude that the equilibrium pressure of the reaction is decreasing faster. This hypothesis is consistent with the general trend of more negative free energies of reaction with decreasing temperature noted for the thermodynamic calculations of various perovskite systems.

One other interesting observation regarding the surface area enhancement is as follows. In the cases where the hydration or carbonation procedure enhanced the surface area, a large fraction of the surface area enhancement was evident after hydration (or carbonation) and prior to dehydration (decarbonation).

X-Ray Diffraction Studies

We used x-ray diffraction to qualitatively study the structure of the mixed metal oxides. We used a Debye-Scherrer camera to measure the d spacings of the mixed metal

oxides before and after the surface area enhancement procedure. We will concentrate our discussion on the SrZrO_3 and LaCoO_3 results.

The X-ray results for the SrZrO_3 exhibit several additional lines in the post decarbonated sample compared to the reference file and the "as received" sample. Although we did not attempt to determine the source of these extraneous lines, we presume they occur from oxides or carbonates of Sr and Zr resulting from the pressure carbonation procedure. An attempt was made to convert the decarbonated sample to the original perovskite sample by passing oxygen over the sample at 400°C for two hours. Some of the extraneous lines are indeed removed. Additionally, the parent perovskite line of $d = 1.098$ did reappear after oxygen treatment. However, many unaccounted for lines still remain in the pattern. The oxygen treatment only slightly decreased the surface area from 50 to $47 \text{ m}^2/\text{g}$. Possibly, further oxygen treatment or decarbonation in flowing oxygen may result in the perovskite structure while maintaining high surface area.

The X-ray diffraction results for the LaCoO_3 sample in the "as received" and dehydrated state as well as the reference file are shown in Table 2. This sample was hydrated at 200°C and resulted in a surface area increase from 2.6 to $18 \text{ m}^2/\text{g}$. The dehydrated sample X-ray pattern exhibits good qualitative agreement with the "as received" and reference file pattern. Due to the nature of the Debye-Scherrer technique, only qualitative peak positions are determined and limited information regarding peak intensity and shape are available. In order to gain more information regarding these samples, Dr. J. Singer of NASA Lewis Research Center conducted experiments using an x-ray diffractometer.

The diffractometer traces for LaCoO_3 "as received" and after dehydration are presented in figures 5 and 6, respectively. The trace in figure 5 for the "as received" sample exhibits well defined peaks predominately corresponding to the perovskite. There is some evidence of lanthanum hydroxide in the parent pattern (ref. 7). In the dehydrated diffractometer trace the peaks occur at the same positions as in the parent pattern as was also observed in the Debye-Scherrer patterns. This indicates that no impurity phases were formed during the pressure hydration and dehydration procedures. The diffraction peak in the dehydrated sample also exhibit considerable line broadening and lowering intensity relative to the parent pattern. This most probably results from the smaller crystallite size of the dehydrated sample (ref. 7), consistent with the increase in surface area from 2.6 to $18 \text{ m}^2/\text{g}$.

Our presumption for the surface area enhancement mechanism involved the formation of an hydroxide during pressure hydration. This has not been confirmed and other mechanisms for the surface area enhancement may be possible. In order to gain insight into the mechanism, we suggest more extensive characterization of the perovskites at different stages of pressure hydration/dehydration.

Electrochemical Activity Measurement

A set of rotating electrode experiments addressed the change of electrochemical activity with enhanced surface area for the mixed metal oxide LaCoO_3 . We conducted three rotating electrode experiments using powder disc samples. The electrocatalyst powders were Vulcan XC-72 obtained from Cabot corporation, LaCoO_3 "as received" from ChemMaterials, and LaCoO_3 hydrated at 200°C and dehydrated at 400°C with the resultant surface area of $18 \text{ m}^2/\text{g}$. The disc samples with the perovskite contained 90 percent Vulcan XC-72 and 10 percent LaCoO_3 powder plus 20 percent Teflon as a binder.

We present the disc current data for these three electrodes at a rotation rate of 1600 rpm in figure 7. The potential sweep range used did not allow the establishment of a well defined limiting current for the perovskite samples and should have been extended in the cathodic direction. All three samples exhibit a plateau at approximately 0.7V versus RHE which may be attributed to hydrogen peroxide production. The activity of the "as received" perovskite (i.e., 10 percent LaCoO_3 and 90 percent Vulcan XC-72) is essentially the same as that of the Vulcan XC-72. However, in the case of the surface area enhanced LaCoO_3 , the oxygen reduction current is substantially increased over the entire potential range studied. This validates our approach of increasing the activity of mixed metal oxides by increasing their surface area.

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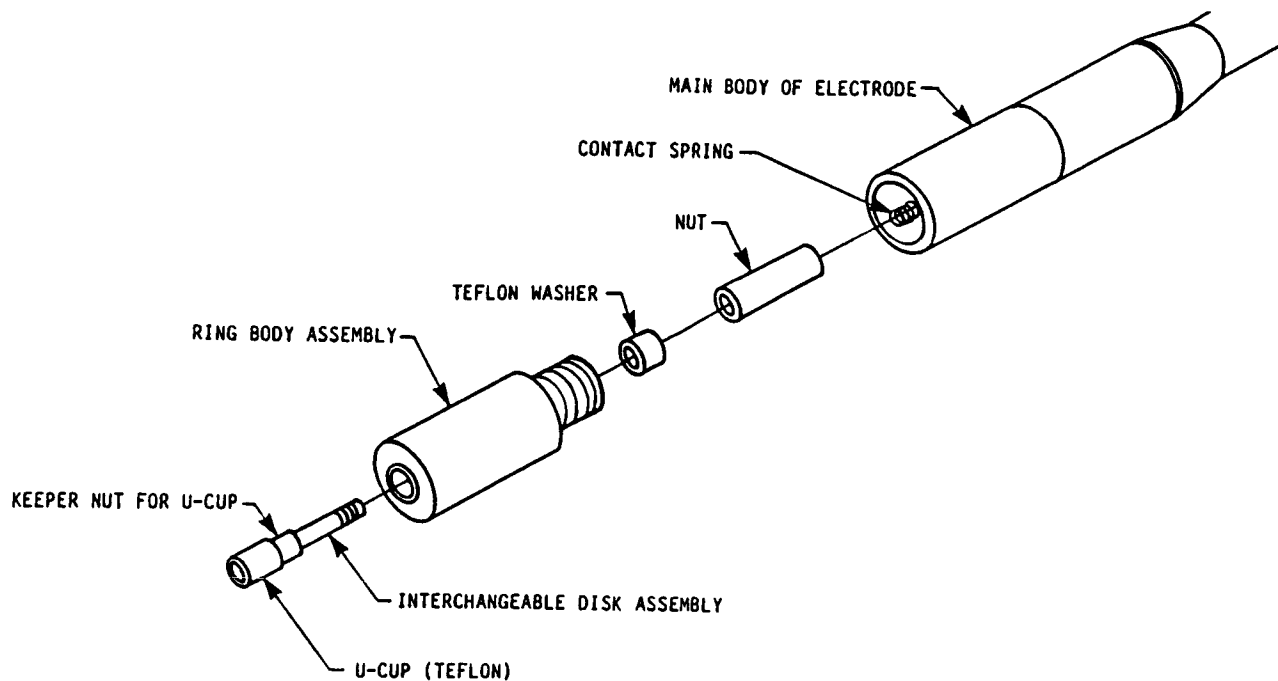
Table 1. - Surface Area Data for Mixed Metal Oxides
(All Values in m²/g)

Material	As Received	After Hydration/ Dehydration	After Carbonation/ Decarbonation	Enhancement Factor H ₂ O/CO ₂
La ₂ CuO ₄	0.96	3.23	0.74	3.4/
La ₂ O ₃ ·2TiO ₂	1.74	2.25	1.84	
CaTiO ₃	3.36	3.65	3.65	
MgTiO ₃	3.67	11.33	3.98	3/
SrTiO ₃	2.32	2.55	2.29	
SrZrO ₃	3.91	6.64	50.58	/13
Pb ₂ Ru ₂ O ₇	31.2	19.31	34.11	
SrLaNiO ₄	2.22	11.42	2.56	5/
La _{0.5} Sr _{0.5} CoO ₃	1.05	1.33	1.28	
La _{0.7} Sr _{0.3} MnO ₃	7.62	8.63	9.15	
La ₄ Ni ₃ O ₁₀	0.70	4.31	1.92	6/2.7
LaNiO ₃	0.45	1.11	0.46	2.5/
LaCoO ₃	2.59	4-18	2.63	1.5-7/
La _{0.5} Sr _{0.5} MnO ₃	10.1	10.68	9.81	
CoMn ₂ O ₄	1.81	2.24	2.68	
MgO·ZrO ₂	3.61	79.38	35.84	22/10

Table 2. - XRD by the Debye-Scherrer Method for LaCoO₃ (hydration 200°C)

Line	File Number 10-268		As Received d(Å) 2.59 m ² /g	Post (-H ₂ O) d(Å) 18.11 m ² /g
	d(Å)	I/I ₀		
1	3.82	20	3.79	3.87
2			3.43	3.27
3	2.734	100	2.70	2.75
4	2.682	87	2.66	2.69
5	2.281	10	2.23	2.45
6	2.214	24	2.18	2.24
7	1.910	55	1.90	1.90
8	1.566	38	1.57	1.56
9	1.547	17	1.54	1.55
10	1.360	20	1.35	
11	1.344	25	1.34	
12	1.214	20	1.21	
13	1.205	20	1.21	
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15	1.091	4	1.03	
16			1.02	
17			1.02	
18			1.01	

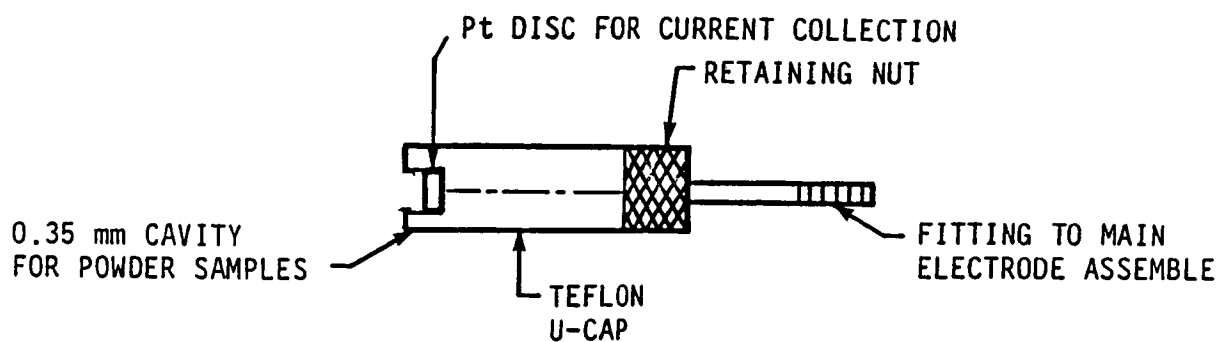
Demountable Rotating Ring Disc Electrode Assembly from Pine Instrument Co.



A-3769

Figure 1.

Stem Containing Cavity for Powder Electrocatalysts Samples



A-3866

Figure 2.

BET Surface Area of LaCoO_3 as a Function of Hydration Pressure

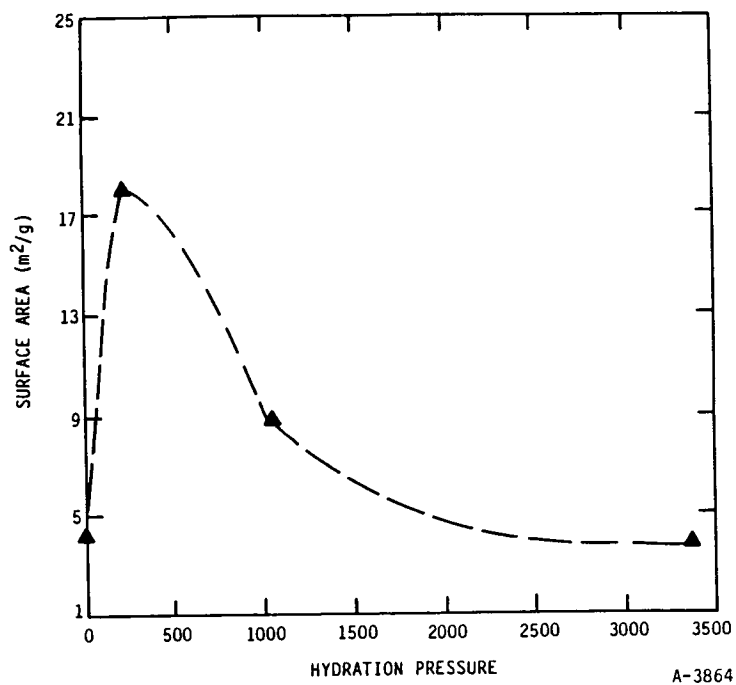


Figure 3.

BET Surface Area of LaCoO_3 as a Function of Hydration Temperature

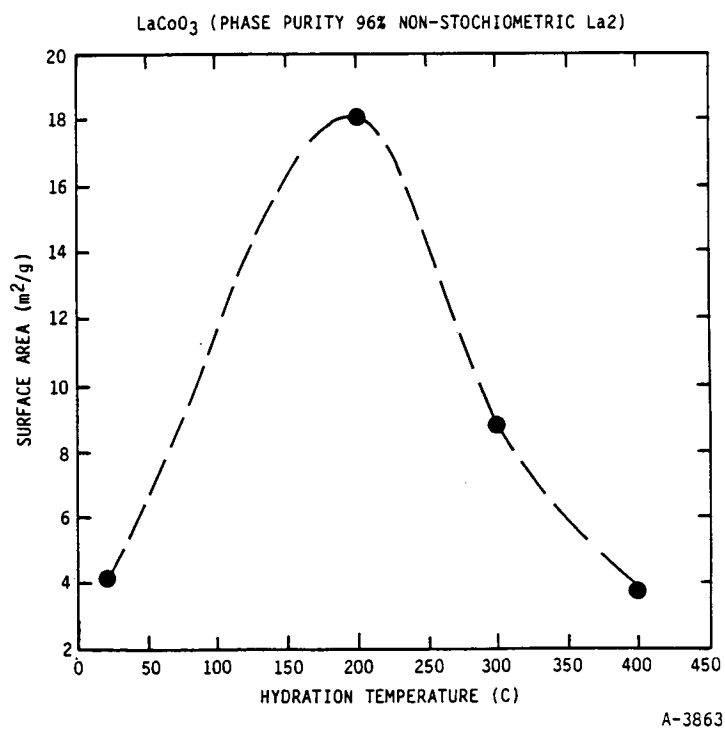


Figure 4.

Diffractogram of LaCoO_3 "As Received"

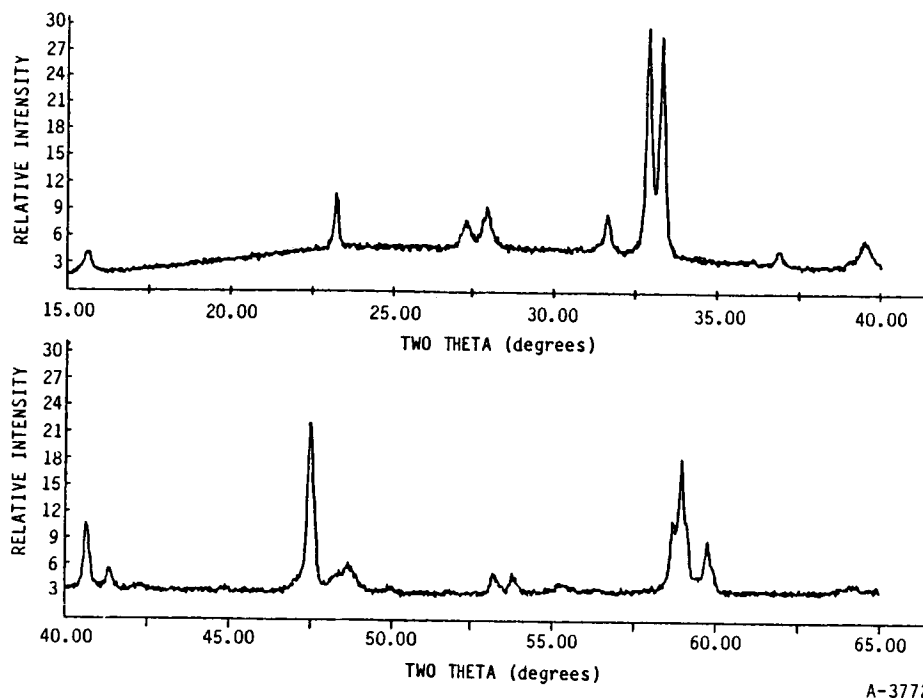


Figure 5.

Diffractogram of Enhanced Surface Area LaCoO_3

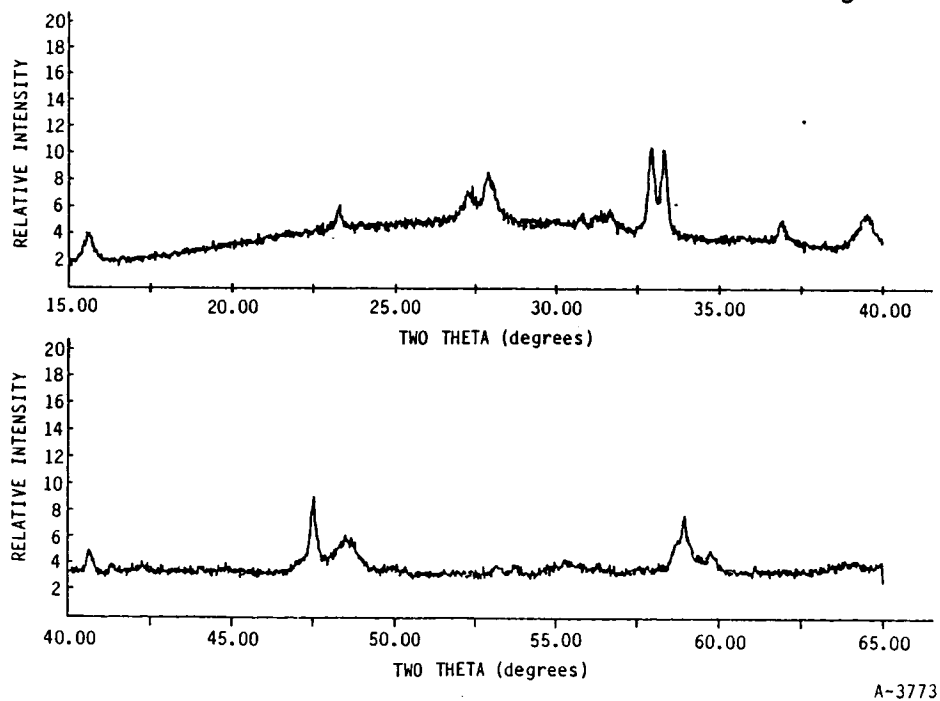


Figure 6.

Oxygen Reduction Current for Vulcan XC-72, 10 Percent LaCoO₃ (As Received)
+ 90 Percent Vulcan XC-72, and 10 Percent LaCoO₃ (Expanded)
+ 90 Percent Vulcan XC-73

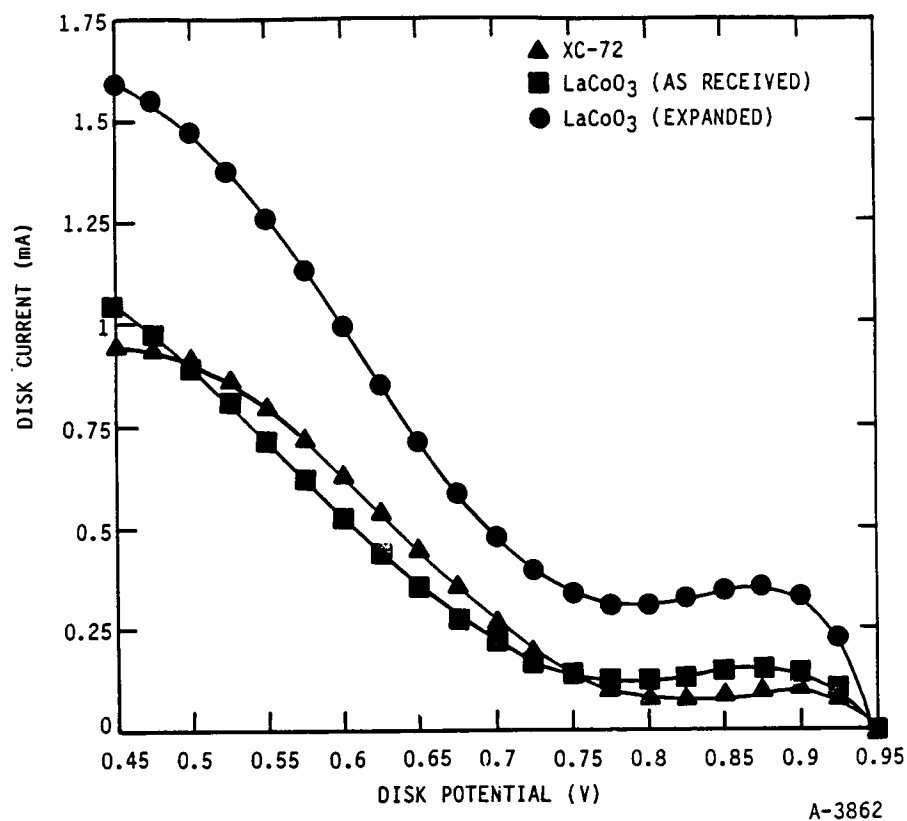


Figure 7.