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Date: February 14, 1995

Subject: Annual Report to the University of California
(Los Alamos National Laboratory ID#: 9-XV3-8249J-1)
Catalysts and Electrocatalysts for the Selective Oxidation of Propylene

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Please find attached a summary of the status of our work on three topics:

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- a) Synthesis and characterization of the Mn doped bismuth vanadates
- b) Electrode studies
- c) Oxygen permeation

I also attached, three reports that have been written acknowledging support from LANL. I anticipate several others as we complete the detailed studies of the Mn doped bismuth vanadates. I will forward these to you as they are submitted. I have enjoyed working with you and hope that we can continue some interactions.

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a. Manganese Doped Bismuth Vanadates

We have made a detailed study of manganese doped bismuth vanadates with the general composition $\text{Bi}_2\text{V}_{1-x}\text{Mn}_x\text{O}_{5.5-8}$. These compounds are one member of a family of phases that are derived from $\text{Bi}_2\text{VO}_{5.5}$ by partial substitution of vanadium atoms with other transition metals. The entire series are unusual and important because of their very high oxide ion conductivity. We have focused on the Mn system because a significant component of electronic conductivity (required for a good electrode material) is also anticipated. The phase diagram of $\text{Bi}_2\text{V}_{1-x}\text{Mn}_x\text{O}_{5.5-8}$ has been investigated by diffraction and thermal analysis and we have found that the tetragonal phase can be stabilized in the composition range $0.1 \leq x \leq 0.25$. The average structures of the solid solutions have been investigated by both powder X-ray and neutron diffraction. The X-ray data are dominated by scattering from Bi and provide little information other than the cell size and symmetry. We have obtained neutron data on several compositions and results for one composition are shown in Figure 1. The data were modeled with an average structure in space group $I4/mmm$. The fit is excellent though the average disordered structure does not properly represent the local vanadium coordination. In contrast, we have been less successful in fitting the data at other compositions and we have reason to suspect that the thermal treatment can produce significant changes in the local structure. The effect of thermal treatment is also apparent in EXAFS measurements. Distinct differences in the local manganese environment were observed in two samples prepared by different procedures even though they had been annealed at the same final temperature. Microprobe analysis showed no evidence for inhomogeneity on a large scale. Consequently, we believe that significant microscopic differences in metal ion distributions occur for different heat treatments accounting for the EXAFS results and the problems with fitting the neutron data. More extensive studies on quenched samples are needed to work this out. The XAS experiments indicate that the Mn coordination is probably octahedral and that the vanadium environment is very disordered and noncentric. The fitted bond distances suggest a distorted tetrahedral coordination by oxygen atoms. The current status of the XAS measurements is described in the attached report. The conductivity data for the $x = 0.2$ sample is shown in Figure 2. In comparison with two other "good" ionic conductors very little variation in conductivity with composition is observed. We have also measured oxygen permeation in samples of manganese doped bismuth vanadate. Apparently, the oxygen permeation rate is limited by low electronic conductivity. The permeation rates are lower than observed in other materials (see below).

b. Electrode Studies

We have used ac impedance techniques to study the properties of some electrocatalysts. The objective was to investigate the utility of the technique for obtaining mechanistic information relevant to an electrocatalytic reactor. Our initial studies were of oxygen activation on silver electrodes. These data were relatively easy to interpret in terms of O_2 dissociation as the rate limiting step with an apparent activation energy of 1.14eV. We made several attempts to study the effect of alkali promotion on the electrode performance. Large effects have been observed but the data are not yet reproducible, The results are sensitive to the method used to load the alkali metal promoter. Similar ac techniques have been used to investigate $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ electrodes. As with silver, the measurements as a function of temperature and oxygen partial pressure can be interpreted in terms of the oxygen chemistry. Surface adsorption, surface exchange and bulk diffusion processes can all be separately identified. The utility of ac techniques for study of hydrocarbon processes is a topic for future study.

c. Oxygen Permeation Studies

A simpler alternative to an electrocatalytic reactor is a membrane reactor where oxygen permeates by ionic transport through a mixed electron-ion conductor. The permeation is driven by the oxygen partial pressure gradient across the membrane. We have constructed an apparatus for high temperature permeation measurements and studied one system, the defect perovskite oxide $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFO), in detail. The results are described in the attached papers. Important conclusions of the work are to confirm the high permeation rates at high temperature (a flux of 10^{-6} mol/sec cm^2 is equivalent to 1 cm^3/min cm^2) and to demonstrate that the surface exchange kinetics were rate limiting for this material. As mentioned above, even though $Bi_2(Mn,V)O_{5.5-\delta}$ has very high ionic conductivity at low temperatures the permeation rates are lower than for SCFO. It is likely that the electronic conductivity is limiting but surface effects may also be important. Further studies directed towards separating the various contributions are needed for an improved membrane system. The ultimate objective is to design a system that can operate at a temperature compatible with selective hydrocarbon oxidation

Bi₂O₂(Mn_{0.2},V_{0.8})O_{3.5-x} BT1 data Refined Atom Positions for Bi₂V_{0.8}Mn_{0.2}O_{5.4} in I4/mmm

Atom	Position	x	y	z	Occ.
Bi(1)	4c	0.5	0.5	0.1687(1)	1.0
V(1)	2n	0	0	0	0.77
Mn(1)	2a	0	0	0	0.23
O(1)	4d	0	0.5	0.25	1.0
O(2)	8g	0	0.5	0.0281(4)	0.37(3)
O(3)	4c	0	0	0.1006(4)	1.02(3)

Bond Distances (Å)

V(1), Mn(1) - O(2)	2.003(2)
V(1), Mn(1) - O(3)	1.561(6)
Bi(1) - O(1)	2.3267(9)
Bi(1) - O(2)	2.929(5)

Refined Composition

Bi₂V_{0.77}Mn_{0.23}O_{5.52} Figure 1. Neutron Diffraction Results for Bi₂V_{0.8}Mn_{0.2}O_{5.5-8}

Figure 2: A Comparison of the Conductivity of $\text{Bi}_2\text{V}_{0.8}\text{Mn}_{0.2}\text{O}_{5.5}$ with YSZ and BE

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