Tungsten Bronze Fuel Cell Catalysts

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The rare earth tungsten bronzes and several transition metal-tungsten mixed oxides have been found to catalyze the electrochemical oxidation of hydrogen in acid media. Their activity is associated with a high magnetic susceptibility. These systems, and other acid stable, electrically conductive tungsten bronzes and oxides are able to catalyze the reduction of oxygen. The limitations of the electrode structure that was used are discussed.

INTRODUCTION

Present hydrocarbon fuel cells are of two types. The first type uses hydrogen or a hydrocarbon fuel directly, oxidizing it electrochemically at the anode of the fuel cell. In the second type, the hydrocarbon is reformed, by means of water or steam, to hydrogen which is electrochemically oxidized, and to lower molecular weight hydrocarbons, carbon monoxide, and carbon dioxide that are discarded. Both types of fuel cell systems have expensive components. In the first type, platinum group metals form the only efficacious catalysts. Noble metals are the only materials, so far reported, that combine catalytic activity at fuel cell electrodes with acid stability. Acid stability is essential as acidic electrolytes are required in the fuel cell in order to reject the carbon dioxide that is formed during the electrochemical oxidation of the hydrocarbon, and also to expel the carbon dioxide from the atmosphere that diffuses into the electrolyte. The reforming type of fuel cell employs alkaline electrolytes and non-noble catalysts but requires a palladium-silver diffuser to admit only pure hydrogen to the anode (1, 2). This paper reports a series of nonnoble catalysts for direct hydrocarbon fuel cells.

The tungsten bronzes, M_xWO_3, where M

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is any one of several metals, and $0 < x < 1$, possess all the desired characteristics of a potential electrocatalyst. They are acid-stable, electrically conductive (3), and in the single case studied can exist with a variation in oxygen stoichiometry (4), indicating that they can gain and lose oxygen readily. The last property indicates that they can participate in the oxygen transfer that occurs during the fuel cell redox reactions.

We found that the recently reported rare earth tungsten bronzes (5, 6) are acid-stable nonnoble anode catalysts. Further, it has been found here that as yet uncharacterized materials that appear to be mixed oxides of different transition elements and tungsten are also acitve anode catalysts.

METHODS

Preparation of catalysts. The same procedure that was used in the preparation of lanthanum and yttrium tungsten bronzes (7) was used to synthesize the rare earth tungsten bronzes and the transition metal-tungsten mixed oxides. A uranium tungsten bronze, with the composition $U_{0.1}WO_3$ was also prepared using the same method, from U_3O_8, W, and WO_3. $W_{18}O_{49}$ ($WO_{2.72}$) and $W_{20}O_{58}$ ($WO_{2.90}$) were prepared by reacting tungsten and tungsten trioxide in the same manner.

Sodium (8), potassium (8), and lead (9) tungsten bronzes were prepared from a mixture of their tungstates with tungsten and

tungsten trioxide at 800°C. Barium tungsten bronze (10) was prepared from $BaCl_2$, WO_2, and WO_3 under an argon atmosphere at 900° while the thallium (11) bronze was prepared from thallium(III) oxide, tungsten, and tungsten trioxide. Cadmium tungsten bronze (12) was prepared either from cadmium metal and tungsten trioxide at 800° or from cadmium oxide, tungsten, and tungsten trioxide at 1000°. All the preparations with the exception of the barium one were made in evacuated sealed tubes.

In one set of experiments, $Na_{0.3}WO_3$ was prepared by electrolyzing a melt of sodium tungstate and tungsten trioxide. In one melt the electrolysis was accomplished with platinum electrodes while in another graphite electrodes were used.

The reagents used for the preparation of the catalysts were obtained from the following sources. Tungsten metal (0.70 μ) and tungsten trioxide (Grade TO-1) were obtained from the Chemical and Metallurgical Division, Sylvania Electric Products, Inc. The rare earth, yttrium, and lanthanum oxides came from the Rare Earth Division, American Potash and Chemical Corporation and were at least 99.999% pure. The remaining reagents were purchased from Ace Scientific. The Group IIIb and the rare earth oxides were ignited for 4 hr prior to use.

Surface area measurements. The surface area of the catalysts was measured after they were powdered and passed through a 325-mesh (44-μ opening) screen. BET methods at liquid nitrogen temperatures with nitrogen gas were used. All surface areas were within 15% of 5 m^2/g.

X-Ray measurements. The instrument used to obtain X-ray diffraction spectra has been previously described (7). The tungsten bronzes prepared here showed the diffraction spectra that one would expect from the structures given in the literature. The X-ray spectra of the tungsten oxides showed the lines reported for $W_{18}O_{49}$ (13) and $W_{19}O_{58}$ (14).

$U_{0.1}WO_3$ was found to be cubic with a lattice constant of 3.812 Å. It has a lustrous blue color, is not attacked by 3.7 M sulfuric acid at 100°C after 4 hr, and has a specific conductivity greater than 100 mhos/cm. It

therefore can be classified as a tungsten bronze (15). The composition limits and the structures of the uranium tungsten bronzes have not been established yet.

The X-ray diffraction spectra of the transition metal–tungsten oxides cannot be assigned to any previously reported compound or mixture of compounds. They probably arise from a single product that has a complex structure. The X-ray spectra of the inactive composition $Ni_{0.2}WO_3$ is identical to that obtained from $Ni_{0.24}WO_3$, which is an active catalyst.

Preparation of electrodes. The catalysts were fabricated into electrodes so that their performance could be evaluated in a fuel cell. One gram of catalyst was ground to less than 325 mesh and mixed with 5% of its weight of Teflon 41 BX emulsion (Du Pont). The resulting paste was pressed onto a tantalum screen which served as a current collector. The entire system was sintered at 300°C for 30 sec.

This electrode preparation procedure was developed to optimize the performance of noble metal catalysts. This structure was designed to provide a porous electrode in which a gaseous fuel and the acidic electrolyte could both be in contact with the catalyst particles. Teflon is used in the electrode to make the structure somewhat hydrophobic. This prevents the electrolyte from wetting the entire surface of the pores, thus preventing the flooding of the electrode structure (16).

Electrochemical evaluation. A porous electrode prepared in the manner described above was inserted into an electrochemical half-cell. The half-cell contained a graphite rod as the auxiliary (driver) electrode while a calomel electrode served as the reference electrode. Either 3.7 M sulfuric acid at 90°C or 14.7 M phosphoric acid at 150°C was used as the electrolyte. Hydrogen, oxygen, and nitrogen were bubbled across the face of the porous electrode and current as a function of the potential was measured potentiostatically. A material was considered to be an active anode catalyst if more current was obtained each time the electrode was run under hydrogen than when it was run under nitrogen, for at least three cycles of

gas changes. Similarly, a catalyst was considered to be active at a cathode if it gave more current under oxygen than under nitrogen each time the gas was changed. Currents were measured for at least 1/2 hr on each gas.

The properties of these catalysts were also examined by a voltage sweep method (17). A mechanical triangular wave form generator was used to produce a linearly varying voltage and an Anatrol potentiostat was used to ensure control of the potential between the catalyst under test and the reference electrode. The resulting voltage–current signals were displayed on an X–Y recorder.

ELECTROCHEMICAL RESULTS

We have found that many of the rare earth tungsten bronzes can catalyze the electrochemical oxidation of hydrogen in 3.7 M sulfuric acid and in 14.7 M phosphoric acid. For example $M_{0.1}WO_3$, where M is Ce, Sm, Eu, Gd, Dy, Ho, and Yb, all show catalytic activity in this reaction. On the other hand, $Lu_{0.1}WO_3$, $Y_{0.1}WO_3$, and $La_{0.1}WO_3$ showed no anodic activity. Ce_xWO_3 and La_xWO_3, where x was varied from 0.04 to 0.14 in increments of 0.02, were also examined. The cerium tungsten bronze was always active while the lanthanum one was inactive. The remaining rare earth bronzes were not examined.

Mixed oxides of some of the transition elements and tungsten having the composition M_xWO_3 also show catalytic activity in the electrochemical oxidation of hydrogen. The following transition metals form active anode catalysts: Ti, V, Cr, Mn, Fe, Ni, Zn, and Zr. The composition Ni_xWO_3 is active when $x \geq 0.24$. When $x \leq 0.2$ no activity is found. The active composition can catalyze the electrochemical oxidation of methanol, in addition to that of hydrogen. The limits for x for the other transition metal systems have not been established yet, but when $x = 0.2$, active compositions are formed in all of the systems.

The electrochemical reduction of oxygen in sulfuric and phosphoric acids is catalyzed not only by the materials discussed above but can be accomplished with the aid of any electrically conductive, acid-stable tungsten–

oxygen system. Thus $WO_{2.72}$, $WO_{2.9}$, and the following tungsten bronzes serve as catalysts for this cathodic reaction, although they are inactive as anode catalysts: $Na_{0.2}WO_3$, $Na_{0.4}WO_3$, $Na_{0.6}WO_3$, $Na_{0.8}WO_3$, $K_{0.5}WO_3$, $Ba_{0.1}WO_3$, $Pb_{0.2}WO_3$, $Tl_{0.19}WO_3$, $Tl_{0.35}WO_3$, $U_{0.1}WO_3$, and $Cd_{0.1}WO_3$.

$Na_{0.3}WO_3$, grown by electrolysis of the melt on graphite electrodes, showed only cathodic catalysis. The sample grown on platinum electrodes gave some anode activity as well. This undoubtedly arises from platinum that migrated into the sodium tungsten bronze.

Figure 1 presents the activity of $Ce_{0.1}WO_3$ on hydrogen and oxygen. It is typical of the catalysis shown by the rare earth tungsten bronzes. Figure 2 shows the activity of $Ni_{0.24}WO_3$ towards hydrogen, methanol, and oxygen. These curves were obtained after the electrodes containing the catalysts had been run for 16 hr on nitrogen. No current was observed under this gas. The nickel composition has been run on hydrogen in sulfuric acid for 4 weeks, 9 hr a day, 5 days a week with no loss in catalytic activity. The electrolyte was let cool at night and was filled to mark once a week with acid to replenish the electrolyte lost through leakage.

Voltage sweep measurements of all the catalysts studied gave essentially the same result. A large double peak anodic current extending from 100 to 400 mV polarization from the theoretical hydrogen potential is found as the voltage is increased from 0 to 1.5 V (anodic sweep). A large cathodic peak is found near the theoretical hydrogen potential when the voltage is returned from 1.5 to 0 V. Those catalysts that show activity towards hydrogen give larger anodic currents when the voltage sweep is conducted under hydrogen than when it is run under nitrogen. All the catalysts give greater cathodic currents under oxygen than when nitrogen is bubbled across their faces during a sweep.

DISCUSSION

The electrochemical oxidation of hydrogen probably requires several steps. It is likely that the following reactions occur:
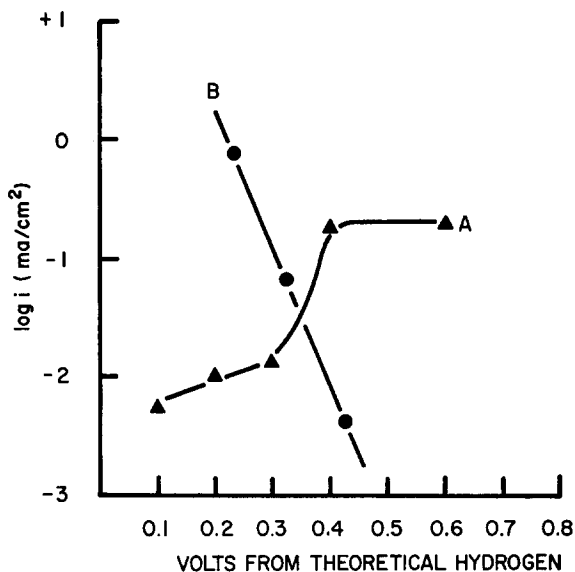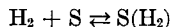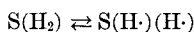
FIG. 1. The electrocatalytic activity of $Ce_{0.1}WO_3$ in $3.7\,M$ H_2SO_4 at 90°C. Curve A, anodic current obtained under hydrogen; Curve B, cathodic current obtained under oxygen.
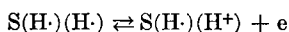
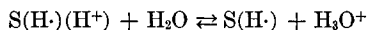Diffusion of hydrogen to the catalyst surface (represented by S) and adsorption onto the surface

$$H_2 + S \rightleftarrows S(H_2)$$

Dissociation of hydrogen on the surface

$$S(H_2) \rightleftarrows S(H\cdot)(H\cdot)$$

Electron transfer to form an adsorbed proton

$$S(H\cdot)(H\cdot) \rightleftarrows S(H\cdot)(H^+) + e$$

Desorption of the proton from the surface

$$S(H\cdot)(H^+) + H_2O \rightleftarrows S(H\cdot) + H_3O^+$$

Jones has found that sodium tungsten bronzes can catalyze the ortho–para conversion of hydrogen and the hydrogen–deuterium exchange in the gas phase (18). Those reactions also involve adsorption and dissociation of hydrogen. Therefore, the lack of activity of sodium and other tungsten bronzes in catalyzing the electrochemical oxidation of hydrogen probably arises from their inability to participate in either the electron transfer or the desorption reaction. As these materials are able to catalyze the electrochemical reduction of oxygen and this process involves an electron transfer step, it appears that these catalysts do not allow the desorption of protons to occur and therefore are not anode catalysts.

In the rare earth, yttrium, and lanthanum tungsten bronzes, M exists in a trivalent state (5, 7). In the lutetium, lanthanum, and yttrium tungsten bronzes there are no unpaired electrons associated with the 12-coordinated ion and the magnetic susceptibility of these tungsten bronzes is quite low. On the other hand, Ce^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, and Yb^{3+} all have unpaired electrons and the magnetic susceptibility of their tungsten bronzes is quite high (5). The latter nonstoichiometric compounds catalyze the electrochemical oxidation of hydrogen while the former cannot. The anodic activity is probably related to the presence of unpaired electrons rather than magnetic susceptibility per se for the magnetic susceptibility of some sodium and potassium tungsten bronzes is high (19) and no activity is found for these systems.

The transition metal–tungsten–oxygen systems are not yet well-characterized and the origin of the catalysis is not yet understood. It appears likely that the transition metal contributes unpaired electrons to a tungsten-oxygen lattice, so that the catalytic activity may be derived from the same source as that of the rare earth tungsten bronzes. If this is the case, then the lack of activity of the cobalt-tungsten-oxygen system is difficult to understand. Cobalt has an electronic
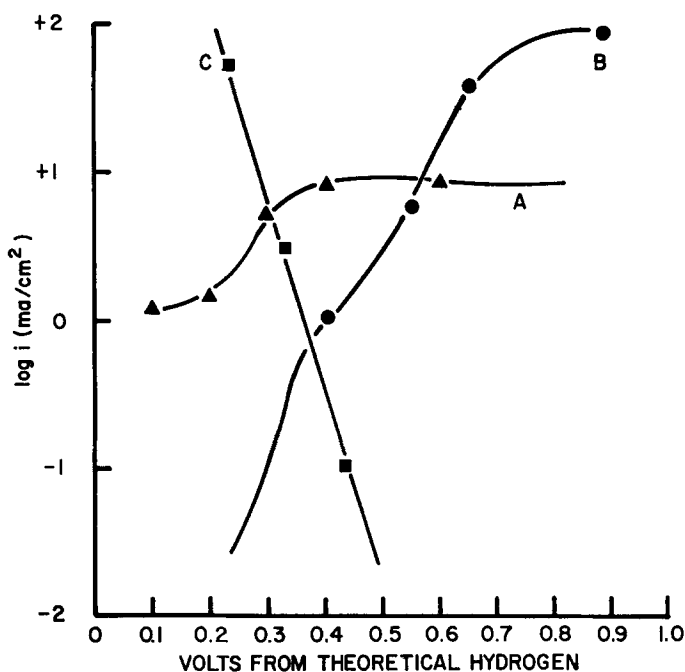
FIG. 2. The electrocatalytic activity of $Ni_{0.24}WO_3$ in 3.7 M H_2SO_4 at 90°C. Curve A, anodic activity under hydrogen; Curve B, anodic activity under methanol; Curve C, cathodic activity under oxygen.

structure between iron and nickel, both of which form active catalyst systems. The activity of Ni_xWO_3 only when $x \geq 0.24$ is also difficult to explain.

The ability to catalyze the electrochemical reduction of oxygen is shown by all the tungsten-oxygen systems that are acid-stable and electrically conductive, whether or not a metal atom is inserted into their structure. These systems probably can exist with a wide variation in oxygen content. They therefore can readily adsorb oxygen and lose it to the solution after it has been reduced.

The current densities shown in Figs. 1 and 2 are several orders of magnitude below those required for practical fuel cells. This poor performance is not a reflection of low catalytic activity, but rather arises from the poor structure of the electrodes used in this work.

Recent work by Bockris and co-workers (20) shows that the oxygen exchange current on sodium tungsten bronzes is greater than that on platinum. These authors have further found that the reduction of oxygen on single crystals of sodium tungsten bronze proceeds at about 10 ma/cm² of geometric surface area at 0.25 V from the reversible hydrogen potential (21). This indicates that the electrodes prepared here have an effective surface area of at most 10 cm²/g of catalyst, as 100 ma/g is the highest current level we have observed at this potential. The low effective surface area of our electrodes may arise from poor electrical conductivity either between particles of the catalyst powder (22) or because the catalyst powder is insulated from the current collector by residual Teflon. The electrodes prepared here have a resistance greater than 1000 ohms between the tantalum screen and the catalyst.

Tafel slopes are not found during the anodic reaction studied here, even at low current densities and low polarizations. This could arise from a limitation on the diffusion of fuel and is further evidence that the present electrode structure is poor.

The existence of two peaks during the anodic part of the voltage sweep indicates that the surface has two adsorption sites (23). The presence of these peaks in catalysts that are not active in the anodic process is

further evidence that these catalysts can adsorb fuel but cannot participate in either the charge transfer or desorption step.

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