

METHANOL FUEL CELLS WITH DISSOLVED OXIDANTS

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Among the desired characteristics of both fuel and oxidant for fuel cells are storability and high energy content per unit weight. The weight must include that of the container. Therefore, the best high-energy fuel and oxidant -- hydrogen and oxygen -- lose much of their advantage in transportable cells, especially if oxygen cannot be taken directly from the air. One of the most easily stored fuels is methanol, and recently the authors developed high-current-density electrodes for the electrochemical oxidation of methanol in alkaline solution (1). Since methanol is soluble in the electrolyte, no multiple porosity is required in the electrode and the active layer may be only 0.01-0.02 cm thick. Thus, as far as fuel is concerned, compact cells are feasible. Matching oxidant electrodes are, however, needed.

The customary porous carbon electrode that is operated with oxygen or air as the oxidant performs very poorly in the methanol-containing caustic since its waterproofing fails in the presence of methanol. In some applications, air may not be available at all and then the weight of bottled oxygen is a handicap; for instance, in the regular large-size oxygen cylinder, one gram equivalent (8 g) of oxygen requires an additional 80 g in the cylinder weight.

Even though all other oxidants have higher equivalent weights, many can be easily stored in solid, dissolved, or liquid form in light containers. Some also have higher oxidizing potentials. Oxidants supplied in dissolved form to the fuel-cell cathode should require only a thin porous layer of an electrocatalyst and no porous bulk electrode in addition to this layer. Thus, compact fuel cells should be possible if a sufficiently electrochemically active alkaline oxidant/electrode system were available.

To find an appropriate system, several oxidants and electrodes were investigated as half-cells. Complete methanol fuel cells were constructed with the most promising oxidant -- chlorite.

II. SELECTION OF OXIDANTS: THEORETICAL

Following requirements were formulated for the selection of soluble oxidants:

- (1) high electrode potential to provide for high cell potential when coupled with the methanol electrode.
- (2) low weight per ampere-hour
- (3) storability in concentrated form
- (4) freedom from obnoxious fumes
- (5) solubility of reduction products
- (6) lack of gas formation in reduction
- (7) electrochemical reactivity
- (8) low polarization.

The first six requirements can be checked by using literature data. The high electrode potential expected may not be realized when the electrode is not a good electrocatalyst. Hence the reactivity and low polarization requirements need experimental study.

Table I lists soluble oxidants with high Gibbs electrode potentials, V° .^{*} The weights are calculated on the basis of sodium salts of the corresponding anions, except for HO_2^- in which H_2O_2 is the oxidant. Since water is generated at the anode, the weight of water is not included in the calculation. Data for oxygen, with the theoretical V° for the four-electron process and for the more realistic two-electron Berl's reaction, are also listed. For comparison, data are shown for Ag_2O , the best solid oxidant used in commercial cells. Oxygen needs a container, and hence the weight per ampere-hour would actually be several times higher. Hypochlorite cannot be stored except in dilute form or as $\text{CaCl}_2(\text{ClO})$; hence its weight index is much poorer than shown. Storage of hydrogen peroxide in concentrated form under normal conditions is undesirable. With the usual easily storable 30% peroxide solution, the weight index is much poorer.

Table I indicates that selection of soluble oxidants of an inorganic nature is rather limited. The open-circuit potential for our methanol electrodes in 5 N KOH is -0.79 volt. Therefore, iodate with $V^\circ = +0.26$ is the last that may be considered in the descending potential series if the complete cell must have a voltage of one volt or higher.

III. SELECTION OF OXIDANTS: EXPERIMENTAL

Although the theoretical electrode potentials for a given oxidant can be high, active low-polarization electrodes for the corresponding reactions may not exist. Soluble oxidants of Table I were studied experimentally in half-cell arrangements. Conventional half-cell polarization techniques, similar to those which have been reported previously, were used.

Polarization characteristics were measured potentiostatically by observing current densities that could be obtained at electronically controlled, preselected, polarized potentials.

* Sign convention recommended by Pitzer and Brewer in 1961 edition of Lewis and Randall "Thermodynamics," p. 356; cf. de Bethune, J. Electrochem. Soc. 102, 288C (1955).

Table I

SOLUBLE OXIDANTS FOR FUEL-CELL CATHODE IN ALKALINE SOLUTION

Calculated from Latimer's
"Oxidation States of Elements," Prentice Hall, 1952

Reaction	V ^o , Standard Electrode Potential Vs S.H.E.	Weight Relations	
		amp-hr/lb	gr/amp-hr
$\text{ClO}^- + \text{H}_2\text{O} + 2e \rightarrow \text{Cl}^- + 2\text{OH}^-$	0.89	325	1.4
$\text{HO}_2^- + \text{H}_2\text{O} + 2e \rightarrow 3\text{OH}^-$	0.88	700 210	0.65 2.15 for 30% soln.
$\text{ClO}_2^- + 2\text{H}_2\text{O} + 4e \rightarrow \text{Cl}^- + 4\text{OH}^-$	0.77	525	0.86
$\text{ClO}_3^- + 3\text{H}_2\text{O} + 6e \rightarrow \text{Cl}^- + 6\text{OH}^-$	0.62	670	0.67
$\text{BrO}_3^- + 3\text{H}_2\text{O} + 6e \rightarrow \text{Br}^- + 6\text{OH}^-$	0.61	470	0.98
$\text{ClO}_4^- + 4\text{H}_2\text{O} + 8e \rightarrow \text{Cl}^- + 8\text{OH}^-$	0.55	780	0.59
$\text{IO}_3^- + 3\text{H}_2\text{O} + 6e \rightarrow \text{I}^- + 6\text{OH}^-$	0.26	360	1.26
$\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^-$	0.4	1500	0.3
$\text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow \text{OH}^- + \text{HO}_2^-$	-0.08	1500	0.3
$2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2$			
$\text{AgO} + \text{H}_2\text{O} + 2e \rightarrow \text{Ag} + 2\text{OH}^-$	0.45	200	2.34

Electrodes included carbon and flame-sprayed thin layers of Raney nickel with or without further platinizing, flame sprayed Raney nickel-silver, and silver. The aluminum-rich phase of alloys was extracted by electrochemical leaching. The platinized Raney nickel corresponded to the high-performance methanol electrodes (4). The bases for the sprayed layers were either nickel sheets or porous sintered-nickel powder plates. Representative results are shown in Table II. None of the oxidants reached the theoretical electrode potentials. Only chlorite and hydrogen peroxide supplied practical current densities at acceptable polarization. Because the chlorite is easily stored and handled, this chemical was selected for further study.

IV. EXPLORATION OF CHLORITE ELECTRODES

Open-circuit potentials and polarization characteristics of flame-sprayed and other electrodes were measured in alkaline chlorite solutions. The effects of chlorite concentration and temperature were studied at the most promising electrodes, flame-sprayed silver, and flame-sprayed Raney nickel-silver. Representative data are summarized in Table II and Figure 1.

The highest values of the open-circuit potential of the chlorite electrode were +0.27 to +0.30 volt, much lower than the theoretical value of +0.77 (Table I). The theoretical value for the $\text{Ag}_2\text{O}/\text{Ag}$

Table II
 EXPERIMENTAL EVALUATION OF OXIDANTS

Temperature, 23°C
 Electrolyte, 5 N KOH

Oxidant	NaClO	NaClO	H ₂ O ₂	NaClO ₂	NaClO ₃	KBrO ₃	NaClO ₄	KIO ₄
Concentration, %	3.8	3.8	3.0	3.0	3.0	5.0	3.0	3.0
Open-Circuit Potential, volts vs SHE	0.48	0.29	0.10	0.29	0.28	0.28	0.15	0.22
Electrode Surface	Carbon	Raney Ni-Ag	Sprayed Ag	Sprayed Ag	Raney Ni-Ag	Raney Ni-Ag	Raney Ni-Ag	Raney Ni-Ag
Current Density, ma/sq cm	1.2							
At + 0.30 volts vs SHE	4.7	41		30		23		
At + 0.20 volts	13.2	55	90	53		27		2.5
At + 0.10 volts	23.0	57	133	83	0.1	28	0.1	7.0
At - 0.00 volts	38.0		140	108	0.2	29	0.1	10.0
At - 0.10 volts			140	137	0.3	30	0.1	
At - 0.20 volts					0.4		0.1	

electrode in 5 N KOH is +0.306; hence, it is likely that the reaction mechanism involves chemical oxidation of silver to Ag_2O by chlorite and electrochemical reduction of Ag_2O . In anodic polarization of the Raney nickel-silver electrode in chlorite solution, heavy currents were accepted with low polarization, apparently with formation of silver oxide. When current was then reversed to begin reduction, approximately equivalent high currents at low polarization could be drawn for a limited time. At continued cathodic polarization, the curves returned to the normal shape of Figure 1. This behavior indirectly supports the $\text{Ag}_2\text{O}/\text{Ag}$ mechanism of the alkaline chlorite electrode.

The data in Table III show that the flame-sprayed silver and Raney nickel-silver gave comparable results. However, the silver electrode appeared to be susceptible to poisoning. The performance often fell after a period of time and could only be restored by electrolytic evolution of hydrogen from the surface. The Raney nickel-silver electrodes were not affected in this manner and were, therefore, chosen for the methanol-chlorite full-cell tests.

Since chloride is the end product of chlorite reduction, the effect of this material on the electrode operation was studied. An electrolyte containing 10% sodium chlorite and 20% sodium chloride was tested and at 55°C showed only a slight decrease in performance due to the chloride. However, at 23°C, the solubility limit was exceeded. Some precipitate was formed, and a severe (75%) decrease in performance was noted.

Addition of small amounts of methanol to a chlorite half-cell did not decrease its performance. Chlorite reduced the performance of a methanol half-cell in a manner similar to that previously noted for chloride (1). It is probable that the chlorite is immediately reduced to chloride by the methanol and then acts as such.

V. EXPLORATION OF METHANOL-CHLORITE FUEL CELL

A. Experimental Work

Full-cell tests were conducted with the following conditions:

Fuel:	160 g methanol/liter 270 g KOH/liter
Fuel electrode:	Flame-sprayed Raney nickel, platinized
Oxidant:	370 g NaClO_2 /liter 270 g KOH/liter
Oxidant electrode:	Flame-sprayed Raney nickel-silver
Temperature:	55°C

The fuel and oxidant compartments were 3 mm thick and were separated by a dialysis membrane (D-30, Nalco Chemical Company, Chicago). The fuel and oxidant were circulated through the cell and were heated externally.

The results of a full-cell test are shown in Figure 2. For comparison, the predicted performance based on the combined best methanol

Table III

EXPERIMENTAL EVALUATION OF CHLORITE ELECTRODES

Electrolyte: 10% NaClO₂ in 5 N KOH

Temperature: 23°C

Electrode	Sprayed Raney Ag-Ni	Sprayed Silver	Platinized Sprayed Raney Ni *	Platinized Platinum *	Carbon
Open-Circuit Potential, volts	0.26	0.27	0.30	0.30	0.10
Current Density, ma/sq cm					
At + 0.20 volts	35	48	1.1	3	
At + 0.10 volts	92	118	6	13	
At 0.00 volts	170	172	25	50	
At - 0.10 volts	280	215	90	104	0.03
At - 0.20 volts		245		200	0.08

* These electrodes are electrochemically active also with methanol.

and chlorite half-cell data is shown. The lower performance of the full cell is probably due to the IR drop in the electrolyte and membrane and possible variations in electrodes. The cell output was 144 ma/sq cm at 0.6 volt.

The efficiency of methanol utilization in this cell was studied in long-term tests. It was found that the number of electrons obtained per methanol molecule approached four at high current densities and fell as current density lowered. This drop is caused by an approximately constant loss of methanol by chemical reaction with the chlorite as a result of diffusion of these across the membrane. At lower current densities this loss became an appreciable part of the total methanol consumption and thus led to a lowered current efficiency for both chlorite and methanol.

B. Weight Projections

The possible utility of the methanol-chlorite cell can be seen from Table IV, in which the output of several types of cells is given in terms of watt-hour/lb. The fuel-cell performance figures are based on the weight of the fuel and containers only. Therefore, the performance figure is a limiting figure approached for long-term use in which the weight of the cell itself becomes small compared with that of the reactants. For short-term, high current-drain applications, the conventional cells occupy a more favorable position than indicated by the table.

Table IV

ENERGY-TO-WEIGHT PROJECTIONS

<u>Conventional Cells</u>	<u>Watt-hour/lb</u>
Lead Storage	10-20
Nickel-Iron (Edison) Storage	15
Silver-Zinc	65
<u>Fuel Cells (weight of reactants and containers only)</u>	
Hydrogen Cell, Air Breathing (hydrogen from sodium borohydride and sulfuric acid)	102
Hydrogen Cell, Air Breathing (hydrogen in light-weight steel container)	70
Methanol Cell - Air Breathing*	300
Methanol Cell - Pressurized Oxygen *	70
Methanol -Chlorite*	140

* Based on 0.7 volt polarized working voltage, 70% current efficiency with 4-electron methanol reaction and with methanol + NaOH as fuel mixture.

It can be seen that the methanol cells show a potential advantage in the weight:energy ratio when compared with the conventional galvanic cells or the hydrogen fuel cells. This advantage exists despite the need for caustic as a fuel component in the alkaline methanol cells. Also compared with cylinder oxygen, chlorite is a more compact form of oxidant. The air-breathing cell is more advantageous on a weight basis but at present suffers from a lower current density.

VI. CONCLUSION

Sodium chlorite has low equivalent weight and favorable electrode potential that combine to make it an interesting oxidant for fuel cell use. It gives useful current densities in alkaline solution at silver-containing electrodes. A methanol-chlorite fuel cell can operate at a current density in excess of 100 ma/sq cm. The easy storability of the fuel and oxidant for such cell results in energy-to-weight ratios that are higher than for cells based on stored gaseous reactants.

VII. ACKNOWLEDGMENT

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LITERATURE CITED

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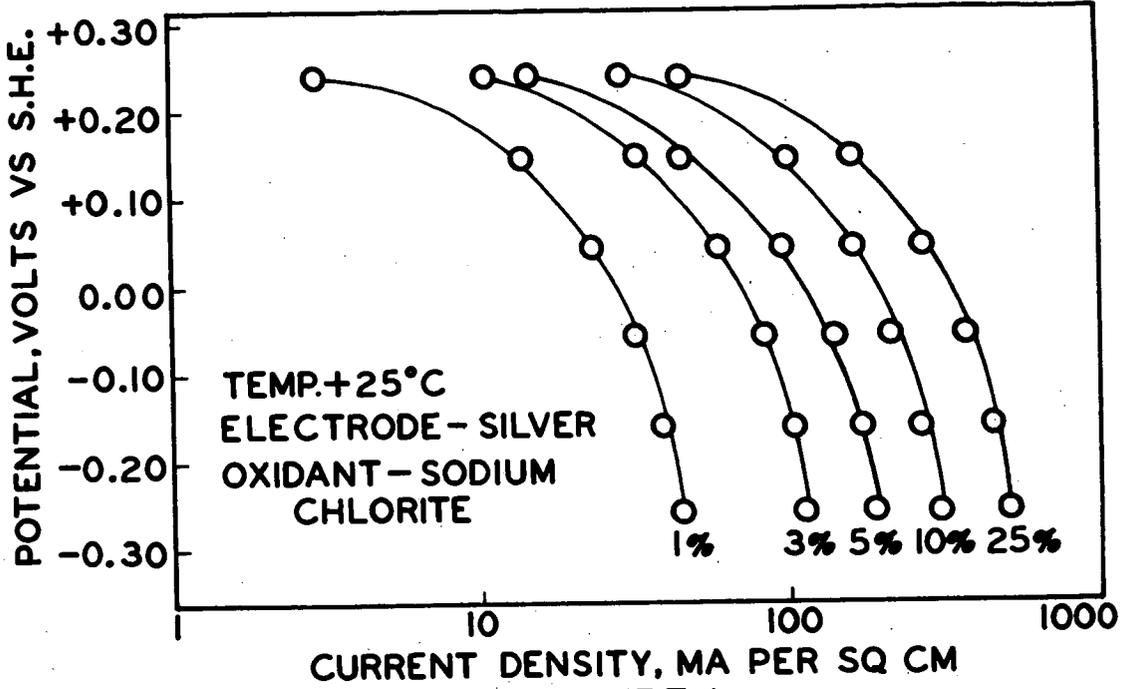


FIGURE 1
EFFECT OF CONCENTRATION

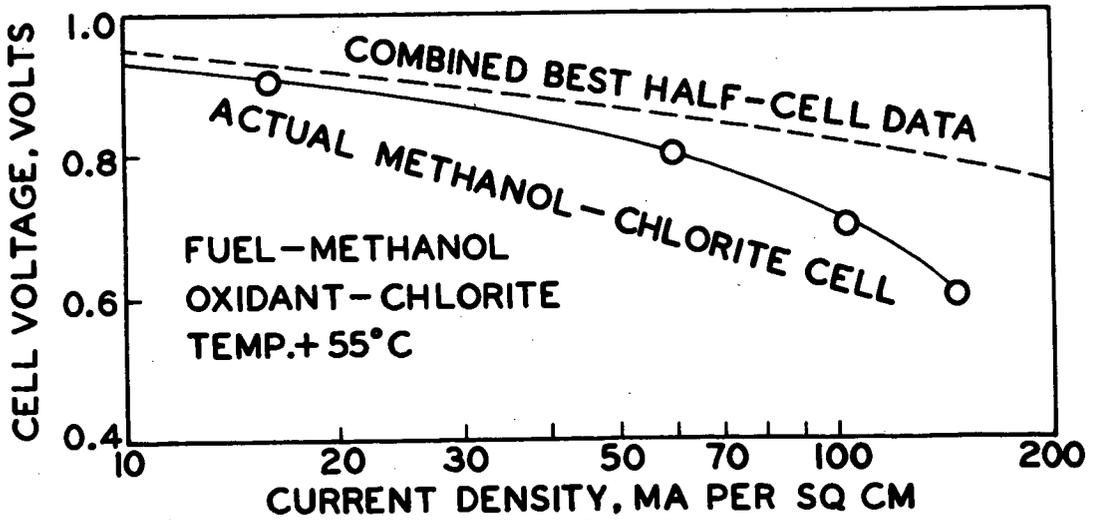


FIGURE 2
FUEL CELL POLARIZATION CURVES