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Solid Electrolyte Aided Direct Coupling of Methane

Solid electrolyte cells have been utilized as electrochemical oxygen pumps to supply oxygen to or from electrode-catalyst surfaces. Recently, the use of solid electrolytes to promote catalysis for a number of reactions has been investigated (*1*). During these investigations, dramatic increases in the oxygen consumption, far exceeding the amount of oxygen supplied through the O^{2-}-conducting electrolyte, have been observed accompanying overall increases in reaction rates. In addition, this effect has been recently demonstrated in oxidative reactions using Na^+-conducting (*2*) as well as proton-conducting solid electrolytes (*3*). This phenomenon, named NEMCA (*n*onfaradaic *e*lectrochemical *m*odification of *c*atalytic *a*ctivity), has been attributed to an effect on chemisorption bonding, and hence the reaction rate constant, by altering the catalyst work function. The catalyst work function is directly proportional to the catalyst overpotential, which is the extent of polarization at the metal catalyst (*2*). Hence, by applying a threshold voltage to a solid electrolyte cell, the catalyst becomes sufficiently polarized, causing a change in both the work function and the reaction rate.

The conversion of methane to ethane and ethylene is a subject of extensive study by a very large number of research groups in the last 7 years (*4*, *5*). Attempts to convert methane into useful raw materials by using solid oxide electrolytes have been separately reviewed (*6*). Recently, a three-electrode cell using Ag and Ni–Zr electrodes on yttria-stabilized zirconia has been used to study the current–voltage relationship during the oxidation of methane at 600–800°C (*7*). The present communication explores the nonoxidative coupling of methane to C_2 hydrocarbons over silver electrodes using a solid electrolyte with major conductivity via protons. An added feature of this investigation is the utilization of the electrolyte as a support in a one-chamber reactor rather than a solid oxide membrane partition in a two-chamber reactor. This design, adapted from Otsuka *et al.* (*8*), simplifies the overall reactor configuration. Using this type of cell, an attempt is made to connect the nonoxidative coupling of methane with the NEMCA phenomenon.

In addition to the one-chamber cell which is schematically shown in Fig. 1a, two other reactor configurations were employed. Figure 1b shows the one-chamber cell, to which a third electrode was added to aid study of the effect of electrode polarization. Figure 1c shows the two-chamber cell which was used for separate evaluation of electrocatalytic contributions at the anode and cathode.

Reactants and products were analyzed using on-line gas chromatography. The electrolyte was of the composition $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (abbreviated as SCY), where α is the number of oxygen vacancies per perovskite-type unit cell. The SCY electrolyte was prepared using a method based upon that of Iwahara *et al.* (*9*) and is described elsewhere (*3*). Electrolyte disks were 0.75 mm thick and 2 cm in diameter. For the cell in Fig. 1c, the SCY disk was sealed to the bottom of a ceramic tube with cement. Using this two-chamber cell, the protonic conductivity of the SCY electrolyte was tested. In one chamber, hydrogen (or methane) was passed and in the other chamber, helium was passed. Current was applied through the electrolyte so that pro-

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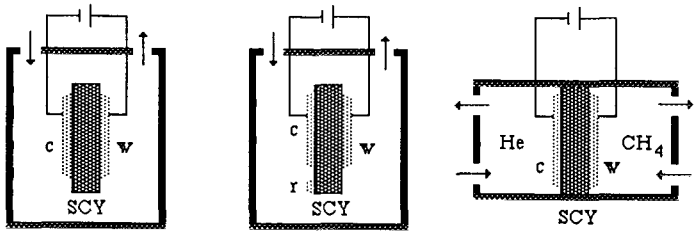

FIG. 1. Reactor cell configurations (not drawn to scale): (a) original two-electrode one-chamber cell, (b) three-electrode one-chamber cell, and (c) two-electrode two-chamber cell.

tons flowed toward the chamber with helium gas. The protonic transfer was analyzed by comparing the current with the rate of hydrogen evolution at the counter electrode which was exposed to the helium gas. The protonic transference number (t_{H+}, defined as the fraction of current carried by protons) was found to be about 0.4 at 700°C when passing dry hydrogen through the chamber. When 4% water vapor was added to the hydrogen inlet, t_{H+} increased to 0.6. The electrolyte may have also partially conducted oxygen ions and electrons as well. The protonic conductivity transfer number did not appreciably change with temperature in the range of 600–750°C. Although the protonic transference number was less than unity, experiments at this time have not proven whether another ionic species, e.g., oxygen ions, could be conducted through the electrolyte. For comparison, a cell similar to that in Fig. 1a was used in which the SCY electrolyte was replaced by yttria-stabilized zirconia (YSZ). The latter is generally accepted to be a pure O^{2-} conductor at the conditions the experiments were run (*10*). The YSZ electrolyte was purchased from Zircoa Products and the specimen tested had a wall thickness of 1.8 mm and a diameter of about 2 cm.

Silver electrodes (G.C. Electronics, suspended in butyl acetate) were painted on the SCY disk. The superficial area of either the anode or cathode was 2.0–3.0 cm^2. The silver electrodes were preheated in air at 400°C for 2 h followed by heating to 750°C for 1 h before actual experiments. The silver film was 25–40 μm thick. The estimated surface area for each electrode-catalyst was 70 cm^2, with an average particle size of 2–3 μm. The electrolyte was placed inside a quartz tube (22 mm I.D.), and wires connected the electrodes to a galvanostat–potentiostat and digital multimeter. The feed stream consisted of pure methane plus a small air leak that corresponded to a feed mole fraction of oxygen equal to 6.5×10^{-4}. The total pressure was 1 atm and the inlet volumetric flowrate was 25 cm^3/min.

Figure 2 shows the rate enhancement ratio ρ versus the total cell voltage at 650 to 750°C. The rate enhancement ratio ρ is that of the rate of methane consumption under closed circuit for a given current or voltage, r, to the rate under open circuit r_0. Figure 2a shows results obtained using the SCY electrolyte at 650 and 700°C. It appears that ρ increased with temperature for constant *overall* cell voltage. The overall cell voltage includes both the overpotential at the working electrode, η_{wr}, and the overpotential at the counter electrode, η_{cr}, as well as the voltage due to ohmic resistance across the Ag|SCY|Ag cell. Figure 2b compares results obtained using the SCY and YSZ electrolytes at 750°C. The increases in ρ appeared with both electrolytes, although more profound rate enhancements were observed with SCY. This observation appears to parallel that of the NEMCA phenomenon

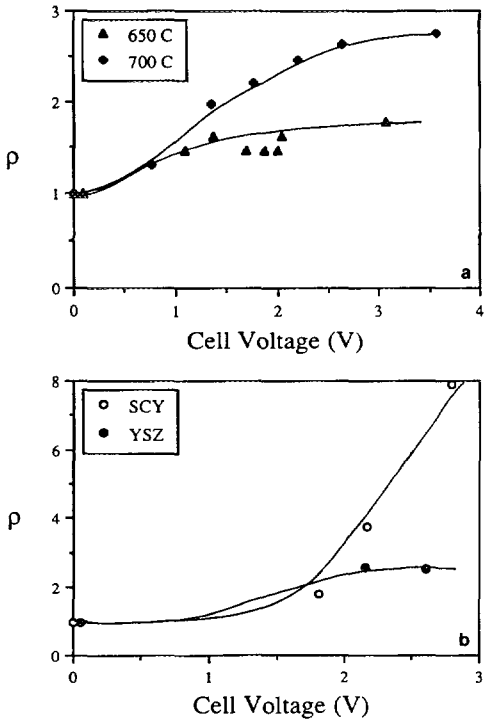

FIG. 2. Cell voltage vs rate enhancement ratio ($\rho = r/r_0$): (a) effect of temperature with SCY electrolyte and (b) effect of electrolyte at 750°C.

where electrocatalytic effects were observed over O^{2-} and Na^+-conducting electrolytes (*1*). The rate of heat evolution due to the ohmic resistance of the cell was experimentally found to raise the temperature at the electrode by no more than 3°C (at I = 50 mA), which cannot account for the eightfold increase in methane consumption (Fig. 2b). Hence, the phenomenon is clearly associated with the electrochemically enhanced production of $CH_3\cdot$ radicals from methane via hydrogen abstraction. Methyl radicals can then easily combine to form ethane, which in turn is dehydrogenated to ethylene (*5*).

Table 1 shows the selectivities and conversions obtained for the data which were obtained galvanostatically, i.e., at constant current. The reported voltages are steady state values attained after a relaxation period of the order of 1 min. The C_2 selectivity was generally 100% except at relatively high currents, where the selectivity dropped to as low as 69% due to some CO_2 formation. No carbon formation was observed. The interpretation of NEMCA suggests that the rate increases were probably not due to a reaction of protons passed through the electrolyte, but to an effect of polarization of the electrodes. In particular, the results obtained with YSZ show that a reaction in which oxygen is not involved stoichiometrically, is enhanced by using a pure O^{2-} conductor.

To further study the effect of potential, it was necessary to use a modified cell, which is that shown in Fig. 1b, where three electrodes were present to allow use of the current interruption method to study the overpotential η at the working and counter electrodes. The third electrode in this case is a reference electrode, equidistant from the other two electrodes. Figure 3 shows a plot of the overpotentials vs $\ln j$, where j is current density at 600°C. The term η_{cr} is the overpotential at the counter electrode and η_{wr} is the overpotential at the working electrode. By definition, upon applying current, protons are passed from the working to the counter electrode. Similar plots were obtained at 650 and 700°C. In Fig. 3, at any given current density, the overpotential, or degree of polarization, at the working electrode was approximately twice that of the absolute value of the overpotential at the counter electrode. In brief, at 600–700°C, the working electrode was always significantly more polarized than the counter electrode.

Since the polarization at the electrodes differed, it was of interest to determine to what degree either electrodes were responsible for the observed rate enhancements. Figure 1c shows the two-chamber cell used to isolate the rate enhancement on the working and on the counter electrodes. Cell current and potential could be applied in either direction. One chamber was exposed to pure methane gas at the working electrode, whereas the other chamber with the counter

TABLE 1

Effect of Temperature and Electrolyte on Rate Enhancement

Solid electrolyte	Temp. (°C)	Cell voltage (volts)	Current (mA)	ρ	C_2H_4 % Selectivity	C_2H_6 % Selectivity	CH_4 % Conversion
SCY	650	1.098	5	1.47	100		0.012
		1.376	10	1.63	100		0.013
		1.700	15	1.47	100		0.012
		2.040	20	1.63	100		0.013
		3.060	40	1.78	100		0.014
SCY	700	0.769	10	1.31	100		0.0155
		1.350	15	1.98	100		0.023
		1.773	20	2.20	100		0.026
		2.206	25	2.46	100		0.029
		2.648	30	2.64	100		0.031
		3.580	50	2.75	85		0.0325
SCY	750	1.81	20	1.82	92.5	7.5	0.019
		2.17	30	3.76	80.7	19.3	0.039
		2.80	50	7.90	53.1	12.1	0.082
YSZ	750	2.15	20	2.58	47.4	52.6	0.170
		2.60	40	2.51	38.3	47.6	0.165

electrode was exposed to He gas. It was determined at 600–700°C that only when current was passed toward the working electrode, and hence protons supplied to the methane-poor chamber, were rate enhancements observed. Reversing the ionic and electronic flow gave no observable increases in rate of methane consumption.

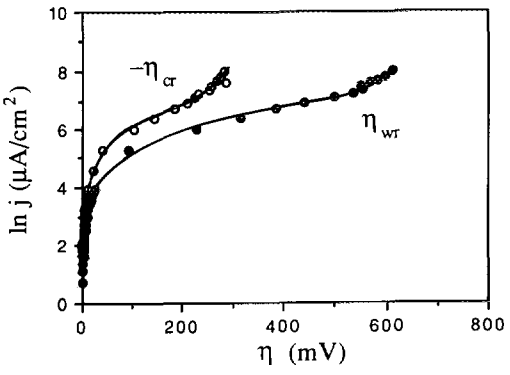

FIG. 3. Overpotential–current density curves at 600°C for electrodes exposed to pure methane. Superficial area of either the counter or working electrode was 2.0 cm^2.

Hence, it is only the anodic working electrode which is responsible for electrocatalytic effects. A reaction with this characteristic has been described as an electrophobic reaction during NEMCA (*1*).

The fact that the rate enhancements increase with temperature seems to contradict the general trend (*1*, *11*) of NEMCA studies, where the most profound enhancements were observed at the lowest temperature examined. Nevertheless, this effect can be explained by using the simple equation derived by Vayenas *et al.* (*1*)

$$\ln \rho = \alpha F(V_{wr} - V^*_{wr})/RT, \qquad (1)$$

where α is a constant and the iR-free potential drop V_{wr} is linearly related to η_{wr}. The term V^*_{wr} is a critical value which must be exceeded in order to have rate enhancements, but its exact physical meaning is uncertain (*1*). Apparently, from this equation, if the temperature increases, given V_{wr} does not vary extensively, r should decrease. The results in Fig. 2, however, show total cell voltage—which includes the voltage drop due to ohmic resistance—rather than V_{wr}.

Because the ohmic resistance of the electrolyte decreases with increasing temperature and hence is a more significant contribution to the total cell voltage at lower temperatures, it is a source of apparent contradiction between Fig. 2 and Eq. (1).

The rate of nonoxidative conversion of methane into C_2 hydrocarbons can be considerably enhanced by using an H^+-conducting solid electrolyte. The effect is not as profound as in previous NEMCA studies, but is clearly related to catalyst polarization rather than stoichiometric reaction of the conducting species.

The rate enhancement occurs at the anodic electrode. At the same time, the polarization of this electrode is far more pronounced than that at the cathode. This observation is in agreement with the NEMCA theory, according to which highly polarized electrodes offer high rate increases.

The single-chamber cell adopted in this study is easy to apply to existing catalytic processes since it does not require reactants to be separated. The metal catalyst can be deposited on the solid electrolyte simply replacing the conventional catalyst support.

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