apart in those cell lines in which we did not detect any myc rearrangement by the Southern blot technique. Thus, other regulatory mechanisms (for example, nucleosome arrangement, DNA methylation, or distantly acting "enhancer" sequences) may be affected by the chromosomal translocation, leading to altered c-myc expression. It is also possible that the rearrangement in the myc locus activates new modes of splicing that generate a defective or fused (30)protein. Such a mechanism, which would generate new species of messenger RNA, has been proposed to occur in mouse plasmacytomas (27-29). However, a preliminary survey of cell lines from undifferentiated B-cell lymphomas displaying a rearranged or nonrearranged cmyc locus revealed no new messenger RNA species (8, 31) and indicated that myc RNA levels are variably increased (8, 31). The significance of this enhanced expression must be confirmed by the analysis of normal cells at the same stage of differentiation.

The frequent involvement of Ig genes in chromosomal translocations characteristic of B-lymphocyte tumors suggests that chromosomal abnormalities may be regarded as recombinational mistakes occurring in genomic regions characterized by high levels of physiologic recombination. These events may be relatively frequent, yet detectable only when they involve genes which, when activated, are able to confer a selective growth advantage to the cell in question. In most undifferentiated B-cell lymphomas the myc gene may be involved when the recombination event involves the region $8(q24 \rightarrow qter)$. However, in several follicular B-cell lymphomas carrying the 14q+ chromosome, one of chromosomes 18, 17, 11, or 12 is the donor chromosome (32). In all these lymphomas the break point on chromosome 14 was located at band q32, probably at the heavy chain locus (27). This supports the speculation that this locus of physiologic recombination may be active in other recombinational events. Other onc genes involved in these recombinations may be identified by exploiting their linkage to Ig loci. **RICCARDO DALLA-FAVERA***

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Methane Synthesis on Nickel by a Solid-State Ionic Method

Abstract. The feasibility of electrochemically synthesizing methane by a Fischer-Tropsch type reaction by use of a solid oxide electrolyte has been demonstrated. This solid-state ionic approach provides in situ control of the oxygen activity at the gascatalyst interface by imposing a suitable voltage drop across an oxygen-conducting solid electrolyte from an external source. Methanation rates for hydrogen-carbon monoxide and hydrogen-carbon dioxide synthesis gas mixtures upon nickel electrodes showed substantial enhancement with the use of this technique, reaching values nearly two orders of magnitude higher than their intrinsic rates.

The scarcity of liquid fossil fuels has created interest in abundant hydrogendeficient materials, such as coal, as alternative energy sources and as chemical feedstocks. Hence, the Fischer-Tropsch and related processes have recently been receiving renewed attention.

The Fischer-Tropsch process consists of the catalytic conversion of H₂ and CO into a large variety of organic compounds. The product distribution is dictated primarily by the operating temperature and pressure, the choice of catalyst, and the H_2/CO ratio.

The kinetic aspects of the Fischer-Tropsch synthesis have been studied extensively (1). However, the nature of the critical reaction intermediate is still debated. Nevertheless, there seems to be reasonable agreement that the controlling feature of the overall rate of the CH₄ formation reaction is the decomposition of CO upon the gas-solid interface. Weakly bonded H₂ competes with the strongly chemisorbed CO for the active sites upon the catalyst surface. Recent spectrographic studies have also indicated that the rate-determining step involves the scission of the C–O bond in the chemisorbed state (2).

Work on related systems indicates that one should be able to use a solid oxide electrolyte to electrochemically decrease the oxygen activity at the gas-catalyst interface to sufficiently low values so that the chemisorbed CO becomes thermodynamically unstable and dissociates, with the oxygen entering the crystal lattice as oxide ions. The oxygen is then "pumped" away from the surface through the solid electrolyte, leaving the active site available for reoccupation. The carbon is then free to react with available hydrogen to form CH₄. Hence, one should be able to influence, and in fact control, the overall net methanation rate by changing the probability of C-O scission and the rate at which the residual oxygen is removed from the catalytic sites.

Experiments have shown that this can be realized by the use of a solid-state ionic device featuring stabilized zirconia, which is predominantly an oxide ion conductor. This solid oxide electrolyte has frequently been used as a "passive" component in solid-state electrochemical cells where the measured open-circuit electromotive force, E, is related to the difference in the activity, a, of oxygen across the electrolyte in terms of the Nernst equation

$$E = -\left(\frac{RT}{4F}\right) \ln\left(\frac{a(O_2)''}{a(O_2)'}\right)$$
(1)

where R is the gas constant, T is the absolute temperature, and F is the Faraday constant.

The "active," as distinct from passive, use of such a device involves in situ control of the oxygen activity at the gascatalyst interface by the imposition of a suitable voltage drop across the electrolyte from an external source. Earlier studies have demonstrated that such a procedure can increase the rate of the decomposition of NO by up to six orders of magnitude (3).

The present work was undertaken to demonstrate the extension of this technique into a different, and technologically important, area—synthesis reactions for hydrocarbon production. The solidstate ionic device constructed for this purpose can be represented by the cell.

$$(-) H_2-CO \text{ or } H_2-CO_2, Ni / YSZ / Pt, air (+)$$
(2)

the description of which is given in (3); YSZ is the yttria-stabilized zirconia, an oxide ion-conducting solid electrolyte.

In order to get appreciable ionic currents, the device must be operated at temperatures at which the solid electrolyte has a sufficiently low resistance. In these initial experiments, the properties and dimensions of the YSZ required temperatures above 600°C. Unfortunately, hydrocarbons are generally not stable at these temperatures. The only exception is CH₄, which is stable up to 600°C. Because of this thermodynamic constraint, CH₄ was the only hydrocarbon product that could be formed under these experimental conditions.

This solid-state ionic device was operated as a differential flow reactor under

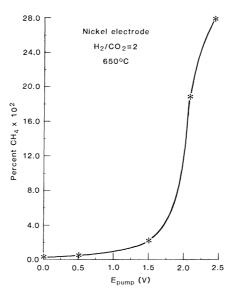


Fig. 1. The dependence of the CH₄ concentration in the effluent gas on the potential imposed across the solid electrolyte (E_{pump}).

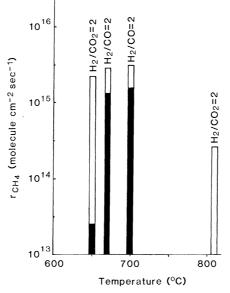


Fig. 2. The effect of the use of this solid-state ionic technique on the methanation rates (r_{CH_4}) of CO and CO₂ on nickel electrodes. The shaded area on each bar represents the intrinsic reaction rate; the unshaded area indicates the electrochemical contribution.

atmospheric pressure, and the conversion rate for CH_4 was kept below 1 percent. The oxygen activity at the gascatalyst interface was controlled by the potential difference imposed across the electrolyte. The air-side electrode (platinum) was always positive, so that reducing conditions were imposed upon the interface in contact with the incoming synthesis gas.

The rates of formation of CH₄ from either H₂-CO or H₂-CO₂ mixtures, determined by the use of gas chromatography, were very dependent on the imposed voltage. Figure 1 shows the variation of the resulting CH₄ concentration on the pump voltage, E_{pump} , defined by

$$E_{\rm pump} = E_{\rm appl} - E^0 - IR_{\rm b} \tag{3}$$

Here E_{appl} is the applied voltage, E^0 is the reversible cell potential, and IR_b is the ohmic voltage drop across the electrolyte.

A substantial increase in the CH₄ concentration in the effluent gas is found only when E_{pump} exceeds 1.5 V. This finding agrees with our earlier observations regarding the electrochemical decomposition of NO on stabilized zirconia (3). The decomposition rate of NO on a bare zirconia surface increased very rapidly when the voltage drop imposed via two platinum point-contact electrodes exceeded about 2 V. We proposed that under those conditions the surface region of the zirconia electrolyte at the cathode terminal becomes partially reduced, thus acting as an in situ mixedconducting electrode with superior catalytic properties.

Similarly, in the present study the negatively charged surface region of the zirconia may also partially reduce and become electronically conducting. The oxygen activity at the gas-catalyst interface for $E_{pump} > 1.5$ V is less than 10^{-30} atm, which is well into the electronic transport regime (4) of this solid electrolyte. Thus both electrons and oxygen vacancies are readily accessible to the chemisorbed CO at the surface of the zirconia. This accessibility enhances the C-O bond scission rate as well as the rate of oxygen incorporation into the crystal lattice and subsequent transport across the electrolyte. Consequently, the rate of CH₄ formation is substantially increased.

The H_2 -CO synthesis gas mixtures intrinsically form CO₂ and H_2O on nickel by the concurrent reverse gasification, Boudouard, and water-shift reactions. Similarly, H_2 -CO₂ mixtures form CO and H_2O . We observed that under electrically biased conditions the CO₂ and H_2O decomposed into CO and H₂. Some carbon deposition on the nickel electrode was also noted. This is in accordance with the thermodynamics of the C-H-O equilibria (5), where all mixtures with H_2/CO ratios smaller than 3 lie within the carbon deposition boundary under these experimental conditions.

The rate of methanation was calculated from the rate of formation of CH₄. The intrinsic catalytic activity of the nickel electrodes for both the CO and CO₂ methanation reactions was determined under open-circuit conditions. Figure 2 shows the dramatic effect of the use of this solid-state ionic technique on the observed methanation rates; the rate of formation of CH₄ from H₂ and CO is twice the intrinsic value. The change is more pronounced in the case of H₂-CO₂ mixtures, which show an enhancement of nearly two orders of magnitude. Methane can be formed at appreciable rates at 810°C, despite its thermodynamic instability and the negligible intrinsic catalytic activity of nickel at that temperature.

The intrinsic rates for CH₄ formation from H₂-CO mixtures were appreciably higher than from H₂-CO₂ mixtures. This finding agrees with earlier results that indicate the difficulty of hydrogenating CO_2 in the presence of CO(1). However, there is no significant difference in the methanation rates from these different gases when the solid-state ionic technique is used. This observation supports recent results (6) which suggest that the same mechanism is critical to the formation of CH_4 from both CO and CO_2 , that is, the dissociation of CO to produce a surface carbon, which then undergoes a hydrogenation reaction. This work illustrates the feasibility of using the solidstate ionic technique to influence the rates of heterogeneous synthesis reactions.

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Demography of Northern Elephant Seals, 1911–1982

Abstract. Northern elephant seals (Mirounga angustirostris) were hunted to near extinction in the 19th century. Protection has allowed them to recolonize former habitat on islands off California, where the population is increasing more than 14 percent per year. Immigration of young pregnant females from Baja California initiated the California rookeries but is responsible for only a small part of recent population growth. Almost 25,000 northern elephant seal pups were born in the species' range in Mexico and the United States in 1982 in comparison with only six known births in 1911.

Effective protection of shore-breeding marine mammals in Mexico and the United States over the last 50 years has allowed northern elephant seals (Mirounga angustirostris) to return to islands off the California coast from which commercial hunting had extirpated them in the 19th century (Fig. 1). This recovery provides an unusual opportunity for quantitative analysis of a population of large mammals recolonizing former habitat after successful conservation.

Elephant seals once bred from north of San Francisco Bay to the tip of Baja California, Mexico. Thought extinct about 1880, the species was rediscovered on Isla Guadalupe, Baja California Norte, in 1892. The world population probably numbered no more than 100 until after 1900 (1).

Transient males visited the California Channel Islands as early as 1925, but breeding began there only after 1950. Eighty pups were seen on San Miguel Island, west of Santa Barbara, in 1958, and 48 on San Nicolas Island in 1959 (2). Adult males appeared on Año Nuevo Island, north of Santa Cruz, in the late 1950's; the first pups were born there in 1961. Pupping began on the Farallon Islands, west of San Francisco, in 1972 (3). Elephant seals have bred on the mainland opposite Año Nuevo Island since 1975 (4). A few breed on Santa Barbara and San Clemente Islands, California, and on the Islas de los Coronados off Tijuana. Elephant seals share the Channel Island chain with five other pinniped species (5).

Single pups are born from December to February. Pups are sedentary and conspicuous, allowing reliable counts of both live and dead animals. Since the entire adult population is not ashore at once, pup numbers are the most satisfactory indicators of population trends. Pups have been counted by different observers at varying intervals on all the occupied islands. This report is based on published data (2, 4, 6-8) and on our recent counts (9) on San Miguel and San Nicolas Islands.

Pup production on San Miguel, San Nicolas, and Año Nuevo Islands has increased at a nearly uniform exponential rate since the end of an initial establishment phase (Figs. 2 and 3). Logarithmic regressions of pup production as a



Fig. 1. Female northern elephant seal (Mirounga angustirostris) and pup on San Miguel Island, California, March 1980. Other elephant seals are in the background.