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TRITIUM TEST OF THE TRITIUM PROCESSING

COMPONENTS UNDER THE ANNEX III US-JAPAN

COLLABORATION

— Annex III Final Report —

March 1993

Satoshi KONISHI, Hiroshi YOSHIDA, Yuji NARUSE
K. E. BINNING*, R. V. CARLSON*, J. R. BARTLIT*
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Tritium Test of the Tritium Processing Components

under the Annex III US-Japan Collaboration

- Annex III Final Report -

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The process ready components for Fuel Cleanup System were tested at the TSTA under the US-Japan Collaboration program. Palladium diffuser for tritium purification and Ceramic Electrolysis Cell for decomposition of tritiated water respectively were tested with pure tritium for years. The characteristics of the components with hydrogen isotopes, effects of impurities, and long-term reliability of the components were studied. It was concluded that these components are suitable and attractive for fusion fuel processing systems.

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* Los Alamos National Laboratory

アネックスⅢ日米協力によるトリチウムプロセス機器のホット試験
－ア ネ ッ ク ス Ⅲ 終 了 報 告－

日本原子力研究所那珂研究所核融合工学部

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原研はDOEとの日米協力協定AnnexⅢに基づいて米国ロスアラモス国立研究所（LANL）のトリチウムシステム試験施設（TSTA）において核融合炉燃料サイクルに用いるトリチウムプロセス機器のホット試験を行った。原研の開発したトリチウムの精製を行うパラジウム拡散器，トリチウム水を分解する電解セルについて，純トリチウムを用いた特性試験，長時間耐久試験，トリチウム存在下での不純物試験を行い，実システムに適用可能な機器を開発すると共に，数々の知見を得た。

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1. Introduction

The objective of the Collaborative Program defined by "ANNEX III to the Implementing Arrangement between the Japan Atomic Energy Research Institute and the United States Department of Energy on Cooperation in Fusion Research and Development for the DOE-JAERI Collaborative Program in Development of Improved Components for the Fuel Cleanup System of the Tritium Systems Test Assembly" (hereinafter referred as Annex III) is to test the two "process-ready" components, the palladium diffuser and the ceramic electrolysis cell, both designed and manufactured by JAERI for the purpose of developing improved components for the Fuel Cleanup System(FCU), which would be applicable to the next generation of fusion experimental devices.

A palladium diffuser separates hydrogen isotopes from all other impurity species and produces a pure hydrogen stream that will be handled in the isotope separation system in the fusion fuel loop. The ceramic electrolysis cell decomposes tritiated water vapor without generating solid waste or having a large tritium inventory. Both components had been developed for application in fusion fuel cycle by JAERI. Since 1984, preliminary tests on both components with tritium have successfully been performed at the TSTA under an early agreement on DOE-JAERI collaboration. Both components proved to be feasible for tritium service and seemed attractive for application in the processes of the Fuel Cleanup. Thus further studies were suggested for development of practical components.

The Annex III agreement on the research and development of the process ready components was signed on November 10, 1986 for two years collaboration and extended for one year in November 1988 for additional testing. Experiments were performed with considerable amounts of tritium at the Tritium Systems Test Assembly (hereinafter referred as TSTA) in the Los Alamos National Laboratory using off-loop apparatus. Personnel are assigned from both JAERI and TSTA to conduct the tests and a number of visits from JAERI for the duration of several weeks each took place. All the experiments were successfully completed by November 1989 when the ANNEX III agreement expired.

2. Management

The Steering Committee that is composed of two members each from both sides was responsible for the management of the program. Implementing plans for experiments and reports of the results were reviewed and agreed to by the Committee. Personnel assignments for each year were discussed and agreed. Table 1 summarizes the personnel assignments for the Annex III activity.The steering committee meetings were held each year.

JAERI assigned several scientists to work on the collaborative program at TSTA. Each stayed for several weeks as listed in the Table 2. LANL assigned necessary personnel to conduct the experiments and equipment maintenance throughout the three year period.

Two components, the palladium diffuser and the electrolysis cell were shipped from Japan in February, 1987. Some additional instruments and equipment were also shipped when necessary. All the shipments were imported under temporary bond that allows the equipment to stay as long as three years followed by return or disposal. Contaminated materials used in the experiments were disposed of by LANL in February 1990. Instruments that were not contaminated in the experiments were shipped back to JAERI.

Three implementing plans that describe detailed test procedures and arrangements were submitted to the steering committee and approved. Tests with tritium were conducted under regular TSTA management.

Table 3 shows the publications on the Annex III experiments.

3. Experiments

3.1 Palladium Diffuser

The palladium diffuser contains 35 fine palladium alloy tubes that selectively permeate hydrogen isotopes. Figure 1 shows the schematic of the diffuser. A mixture of hydrogen isotopes and impurity is separated into a pure hydrogen stream and a bleed stream that contains mostly impurity and some residual unpermeated hydrogen. The diffuser is contained in a double jacket in order to recover tritium permeated from the primary containment that is heated up to 450° C by a heater wire wound on it. The flow diagram of the experiment is shown in Figure 2. One or two metal bellows pumps are used to evacuate the inside of the palladium tube and recirculate the permeated hydrogen into the feed stream. Impurities such as methane and carbon monoxide were added in order to investigate the chemical effect and measure the separation characteristics. Gas samples were occasionally taken from the

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feed or bleed for Raman or mass spectroscopy. Flow rates and pressures were measured at the feed and permeated sides of the diffuser. Tritium was supplied to the experiment from the ZrCo bed. Approximately 2500Ci were used. The experiment was independent of the TSTA main loop and was placed in a separate glovebox.

3.2 Ceramic Electrolysis Cell

The electrolysis cell contains 10 sintered stabilized zirconia tubes that has calcined platinum electrodes at the inside and outside. Figure 3 shows the structure of the cell. Water vapor in the feed gas stream is decomposed at the surface of the inner electrode to form hydrogen/tritium while pure oxygen generates at the outer surface of the ceramic tube.

The test loop consisted of a tritium source, a catalytic reactor filled with hopcalite, a LN_2 freezer, the CEC, a metal bellows pump, and a ZrCo tritium storage bed as shown in Figure 4. Pure or high level tritiated water was formed by oxidation of tritium gas at the hopcalite bed. The water vapor was then collected in a freezer so that regeneration of the freezer in the FCU system was simulated. In some tests, vapor was continuously sent to the cell for decomposition followed by recombination with oxygen from the oxygen side of the cell. Inert gas and deuterium was used as carrier gas in the loop. Effects of impurities such as CO and CO_2 were investigated. The experiment was located in a glovebox in an auxiliary laboratory at the TSTA.

3.3 Zirconium Cobalt Bed

The Zirconium-Cobalt intermetallic compound is a new material developed by JAERI as a substitute for uranium for tritium recovery and storage. Both experiments were equipped with ZrCo beds for recovery, storage and supply of tritium as shown in the figures. Some features of the ZrCo beds were tested in practical tritium service.

4. Results

4.1 Palladium Diffuser Experiment

4.1.1 Permeability Measurement

The permeation flow rates of pure H_2, D_2 and T_2 were measured as the functions of pressures at various temperatures. Examples at 300°C were summarized in Figure 5. Flow rates are expressed in cm^3 per minutes at 0°C, 103kPa. Linear relations are observed between flow rates and differential square root of pressures across the membrane although some deviation at both high and low pressures appeared. Permeability of tritium was approximately one half of that for hydrogen.

4.1.2 Separation Characteristics

A mixture of hydrogen and 10% methane was introduced into the system to measure the separation characteristics of the diffuser. Feed and permeation flow rates were measured as a function of the concentration of hydrogen in the bleed stream. The result indicates that a low concentration of hydrogen in the bleed can be obtained from a feed containing major amount of hydrogen. However the permeation flow rate is much smaller than that in the case of pure hydrogen feed. This is caused by a high partial pressure of impurity in the feed side of the diffuser. Previous numerical study suggests that an increased diffuser length would be desirable for achieving low hydrogen concentration in the output impurity stream. The system was left in a continuous operation mode for months and little change in the separation characteristics was observed.

4.1.3 Tritium Containment

Tritium permeation through the stainless steel shell of the diffuser was measured in order to verify the containment by the secondary vacuum/purging jacket where permeated tritium was collected. The observed permeation rate was as high as the order of 10 mCi/hr, depending on the temperature and history of the diffuser. This value is approximately two orders of magnitude lower than those reported in the literature, probably because of the oxide surface of the steel. No tritium release into the glovebox was observed.

4.1.4 Carbon Monoxide Testing

A high concentration of CO in the stream may be encountered in some applications of the diffuser in tritium processing loops[1]. The diffuser was operated with a T_2-CO mixture for 6 months. Approximately a 10% loss of

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[1] For instance, reduction of tritiated water using shift reaction is of interest in combination with the diffuser for separation of tritium product. In this application, palladium tubes are exposed to CO, and especially at the bleed side, CO concentration will relatively be high.

permeability occurred after the above operation. Oxidation treatment of the membrane followed by hydrogen reduction regenerated the permeability as in Fig.6. This result suggests that the reduction of the permeability might be caused by surface contamination of the palladium alloy membrane. A possible deposit of carbon caused by the radiolysis of CO was suspected.

4.1.5 Long-term Reliability

The diffuser was operated at relatively low temperature (150°C ~ 300°C) to investigate the effect of ^{3}He formed in the palladium metal. Little degradation of the permeability was observed in more than 1 year of operation.

4.2 Ceramic Electrolysis Cell Experiment

4.2.1 Decomposition Characteristics

Decomposition characteristics of the electrolysis cell was measured with H_2O-N_2, T_2O-N_2, T_2O-D_2 systems under the conditions simulating application for a plasma exhaust process. In the Fuel Cleanup Systems in TSTA or TPL, DTO captured at the DTO freezers should be regenerated and decomposed to recover tritium. Carrier gases such as N_2, He or D_2 may be used for regeneration of the freezers. Carrier flow rate was 400 - 1000cc/min, where no effect of the flow rate was observed on the characteristics of the cell. Figure 7 shows the conversion efficiency of water vapor to hydrogen obtained with the cell operated at 600°C. Conversion ratio was determined from the ratio of the inlet and the outlet humidities. The Ir-free voltage is measured between the two electrodes on the cell that composes an open circuit where no current is applied. This value indicates the electrochemical potential across the cell generated by the difference of oxygen potential at the O_2 side and the T_2/T_2O side. The observed conversion efficiency was around 95%. These values are lower than expected, probably due to the error caused by the residual humidity at the outlet of the cell. A small isotopic difference was observed between T_2O and H_2O. The theoretical conversion efficiencies for each system are also shown on the figure. The results show similar trends although marked deviations are observed.

Deuterium was tested as carrier gas for the tritiated water. Use of the D_2 for regenerating the freezer is advantageous because only gaseous hydrogen isotopes $(DT)_2$ is expected to be obtained as product stream from the cell. The experiment proves that T_2O can be decomposed at high efficiency at 1.4V, that is higher than the case with inert carrier as predicted by the calculation.

4.2.2 Impurity Testing

Systems of CO_2-N_2 and CO_2-D_2O-N_2 were tested to investigate the effect of CO_2 that might be electrolyzed by the cell while water is decomposed. A thermochemical calculation was made for the electrochemical equilibria of the CO_2, CO, H_2O, H_2, C and O_2 systems in the cell. Figure 8 summarizes the temperature dependencies of the standard voltage, $E°$, for each reaction that is derived from the standard ΔG for the reactions at the temperature,

$$E° = (RT/vF)\Delta G$$, where R is the gas constant, T is the temperature, v is the charge number involved in the reaction, and F is the Faraday constant. Each line shows the standard energy for the equilibrium of each reactions, expressed as the electrochemical potential in Volts. These figures suggest that both reactions of decomposition of CO and CO_2, $CO \leftrightarrow 1/2O_2 + C$, and $CO_2 \leftrightarrow C + O_2$ can occur at the operation temperature of the cell.

Figure 9 shows the relationship between conversion ratios for the reactions discussed above and Ir-free potential at 600°C. For the reactions $CO \leftrightarrow 1/2O_2 + C$, and $CO_2 \leftrightarrow C + O_2$, initial concentrations of CO or CO_2 are assumed to be 0.1. Each line shows how the reaction can proceed at the given Ir-free voltage in the cell. As seen in the figure, the decomposition of water is the easiest to occur in the cell, but all the reactions are possible at the potential of 1.3V to 1.4V where the cell is usually operated. Either CO_2 or CO can be decomposed to form carbon as the result of the reaction.

Figure 10 shows the result of the tests with CO_2. The electrolysis of CO_2 starts at about 1.0V, that is close to the calculated voltage for reaction $CO_2 \leftrightarrow 1/2O_2 + CO$, however the conversion ratio was less than 3%. It is understood that the porous platinum electrode does not have catalytic activity for the decomposition of CO_2 , while it does for the decomposition of water. Electrolysis of D_2O - CO_2 - N_2 mixture shown in the figure indicates no effect on the electrolysis performance of water. These results suggest that CO_2 impurity in the cell does not have any undesirable effect on the decomposition of water.

4.2.3 Batch Operation

One of the major practical applications of the CEC is the batch processing of a tritiated water gas mixture. A 3.8 liter bottle containing mixture of 300Ci tritium, deuterium, hydrogen and ^3He was attached to the loop. In the test, a mixture of tritiated water and carrier was processed with the cold trap, electrolysis cell and a ZrCo bed to convert tritiated water and recover tritium in a closed loop. More than 99.99% of the water was decomposed and tritium was trapped at the bed in several hours of operation.

It was proved that the CEC is suitable to process relatively small amounts of high level tritiated water in a batch operation.

4.2.4 Long-term Reliability

The electrolysis experiment was performed in a closed loop mode in which oxygen generated at the anode is recycled to the catalytic reactor inlet for recombining with electrolyzed tritium. A test with 3%T_2O - 22%CO_2 -N_2 was performed for one year to evaluate the long term reliability of the cell with tritium and impurity. Operating temperature was 640°C and the potential at the cell was controlled with the potentiostat to 1.3V. The cell has successfully worked for the test period. However an embrittlement of the stabilized zirconia material was detected when the test was completed.

4.3 Zirconium-Cobalt Bed

4.3.1 Equilibrium Pressure of Tritium

Pressure-composition isotherms of the T_2-ZrCo system was measured with the ZrCo bed installed in the CEC experimental apparatus. Preliminary results indicated that the ratio of the equilibrium pressure of T_2 to D_2 is less than 2. It is suggested that the isotopic difference was negligible in the practical use of ZrCo for tritium service. Detailed measurement was done by the program and apparatus under the Annex IV agreement.

4.3.2 Practical Application

Both palladium diffuser and electrolysis cell experiments were equipped with ZrCo beds of 5 liter of hydrogen in capacity. The beds were used for storage and supply of pure and mixed tritium. The recovery of tritium was performed both by absorption of pure isotopes and recycling of the mixture with inert through the bed. These practical experiences of the beds verified that a ZrCo bed is a promising substitute for uranium beds.

5. Conclusion

The experimental program on the "process ready components" under Annex III was completed and all of the objectives were achieved experimentally in the tests performed in these three years. Through the tests, it is concluded that the palladium diffuser is applicable to the processing of plasma exhaust to produce pure hydrogen isotopes for as long as 3 years without any maintenance. Use with carbon monoxide was not a problem. The ceramic electrolysis cell was verified as an attractive component for the decomposition of tritiated water in various processes. Carbon dioxide affected it little. Thus, both process-ready components, the palladium diffuser and the ceramic electrolysis cell, were proved to be suitable for fusion fuel

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processing. Long term reliability and compatibility of the components with tritium and impurity was verified.

Based on the results, an integrated process loop, "JAERI Fuel Cleanup System" that utilizes both components was developed and designed by JAERI for full scale demonstration of the plasma exhaust reprocessing. The system will be tested with simulated fusion fuel in the TSTA main loop in the near future.

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Table 1   Personnel Assignments for Annex III Collaboration.

•JAERI Personnel

Year	period	name
1987	3/16 - 4/3	H. Yoshida
	3/23 - 4/24	S. Konishi
	10/19 - 11/13	S. Ohira(TL1)
	10/26 - 11/6	S. Konishi(TL1)
1988	10/17 - 10/28	Y. Matsuda(TL2)
	10/17 - 11/4	S. Konishi(TL2)
		H. Fukui
1989		S. Konishi

•TSTA Personnel

R. V. Carlson, K. E. Binning, E. M. Jenkins, J. R. Bartlit, J. L. Anderson, and facility operators as assigned.

•Steering Committee Members

Year	period	name
1987	7/27 - 7/29	G. R. Nardella, J. L. Anderson M. Iizumi, Y. Naruse
1988	10/26 - 10/28	G. R. Nardella, J. L. Anderson M. Sakamoto, Y. Naruse
1989	7/17 - 7/19	G. R. Nardella, J. Anderson T. Kodaira, K. Okuno

Table 2. Major Activity on Annex III.

Year	month	Subject
1986	11	Annex III Agreement was signed.
1987	2	Components shipped from Japan.
	3	Installation of apparatus began.
	4	Tritium Experiments were initiated.
	7	Steering Committee Meeting
	10	Impurity Experiment performed.
1988	5	Impurity Testing
	10	Steering Committee Meeting
		Long-term Operation started.
	11	Annex III extended for 1 year.
1989	7	Steering Committee Meeting
	11	Annex III was Completed.
1990	2	Apparatus sent back to Japan.

Table 3. List of Publications on Annex III.

"Results of Tritium Experiments on Ceramic Electrolysis Cell and Palladium
Diffusers for Application to Fusion Reactor Fuel Cleanup Systems,"
R. V. Carlson, K. E. Binning, S. Konishi, H. Yoshida, and Y. Naruse
*Proceedings of 12th Symposium on Fusion Engineering, Monterey, CA,
October 1987.*

"Diffuser and Ceramic Electrolysis Cell for Fusion Reactor Fuel Cleanup
Systems,"
S. Konishi, H. Yoshida, R. V. Carlson, K. E. Binning, and J. L. Anderson
presented at *3rd Topical Meeting on Tritium Technology in Fission,
Fusion, and Isotopic Applications, Toronto, Canada, May 1988.*

"Experiments on a Ceramic Electrolysis Cell and a Palladium Diffuser at the
Tritium Systems Test Assembly,"
S. Konishi H. Yoshida, H. Ohno, Y. Naruse, D. O. Coffin C. R. Walthers,
and K. E. Binning,
Fusion Technol., **8**, #2, 2042(1985).
(Studies previously performed under letter exchange.)

"Tritium Experiments on Components for Fusion Fuel Processing at the
Tritium Systems Test Assembly,"
S. Konishi, R. V. Carlson, E. E. Binning, H. Yoshida, J. R. Bartlit, J. L.
Anderson, and Y. Naruse,
to be presented at the *Ninth Topical Meeting on the Technology of Fusion
Energy, Oak Brook, IL Oct 7-11, 1990*
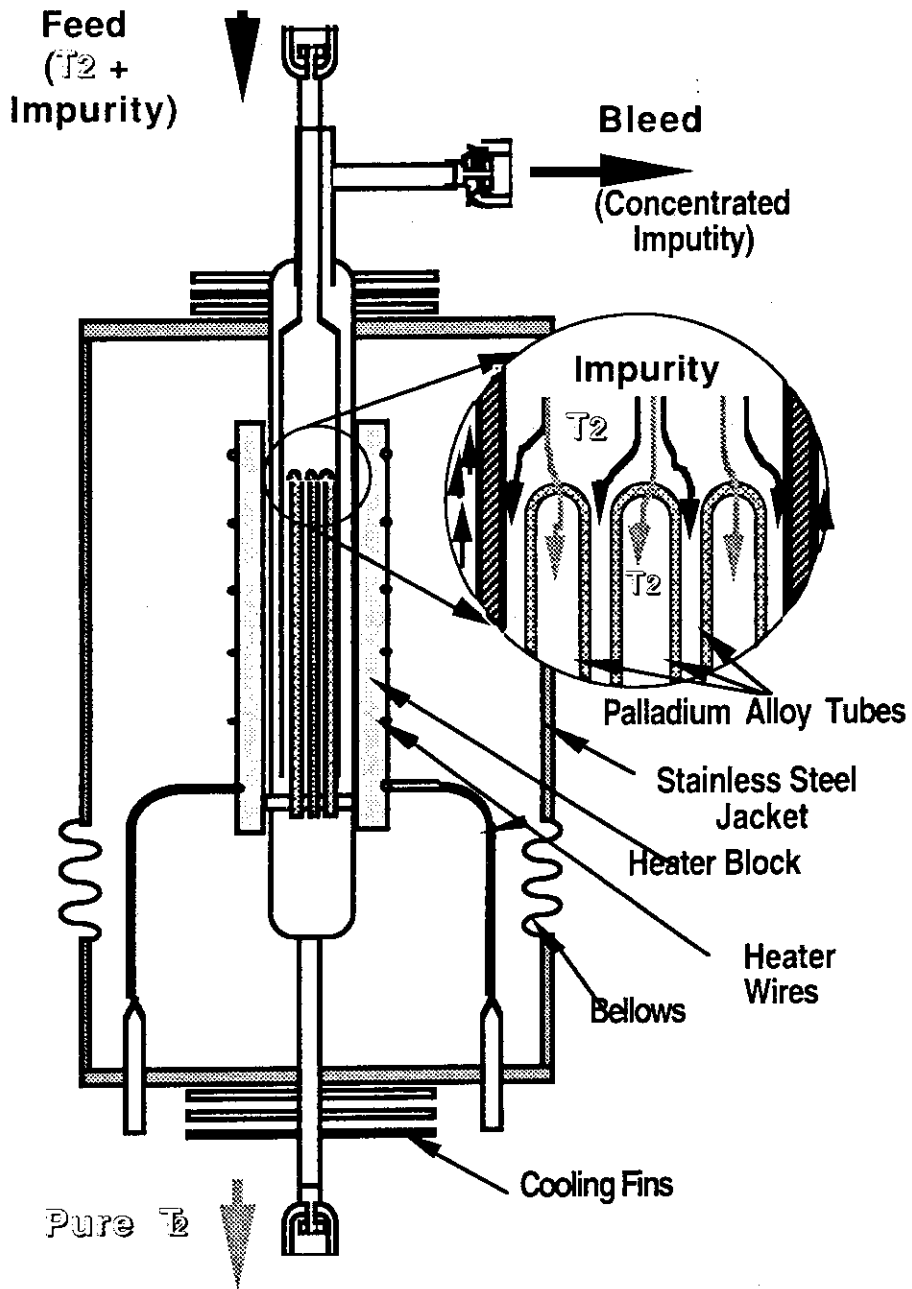
Fig. 1. Schematic of the palladium diffuser.
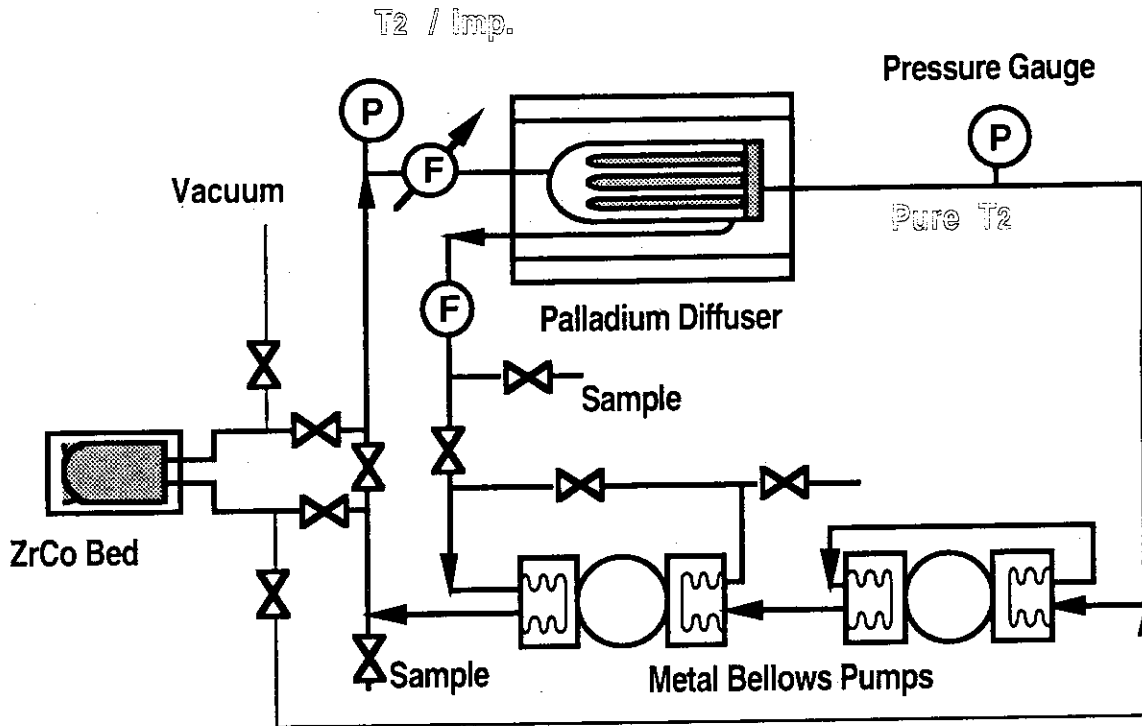
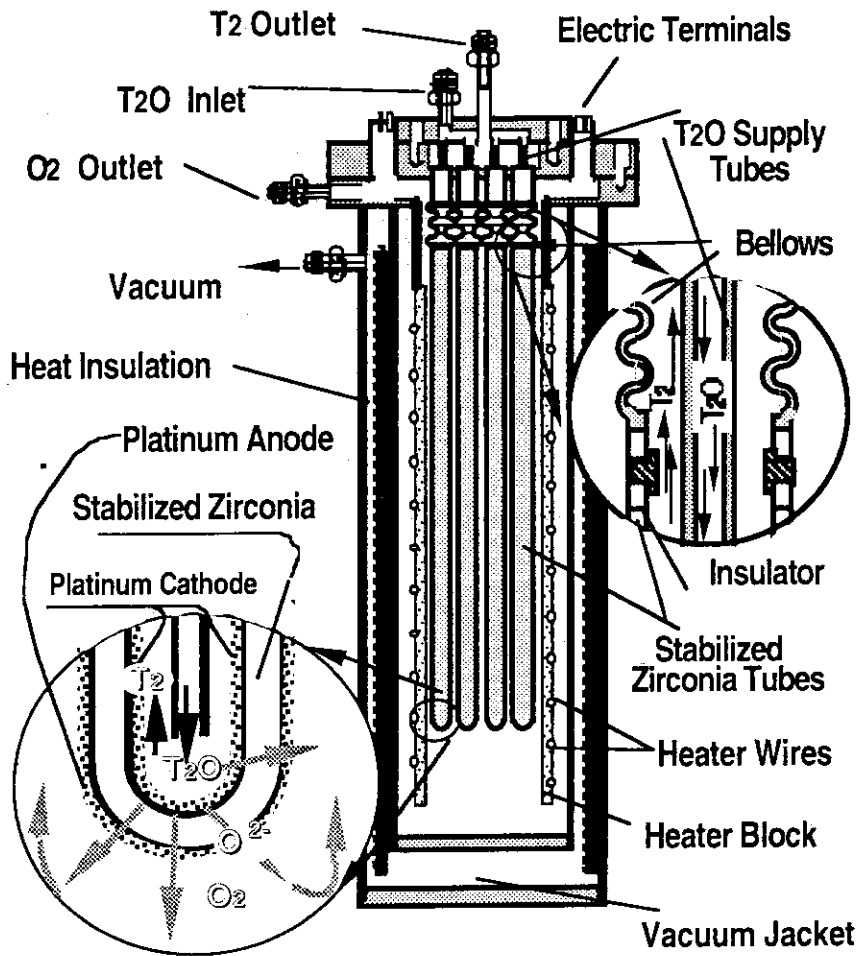Fig. 2. Flow diagram of the palladium diffuser experiment.
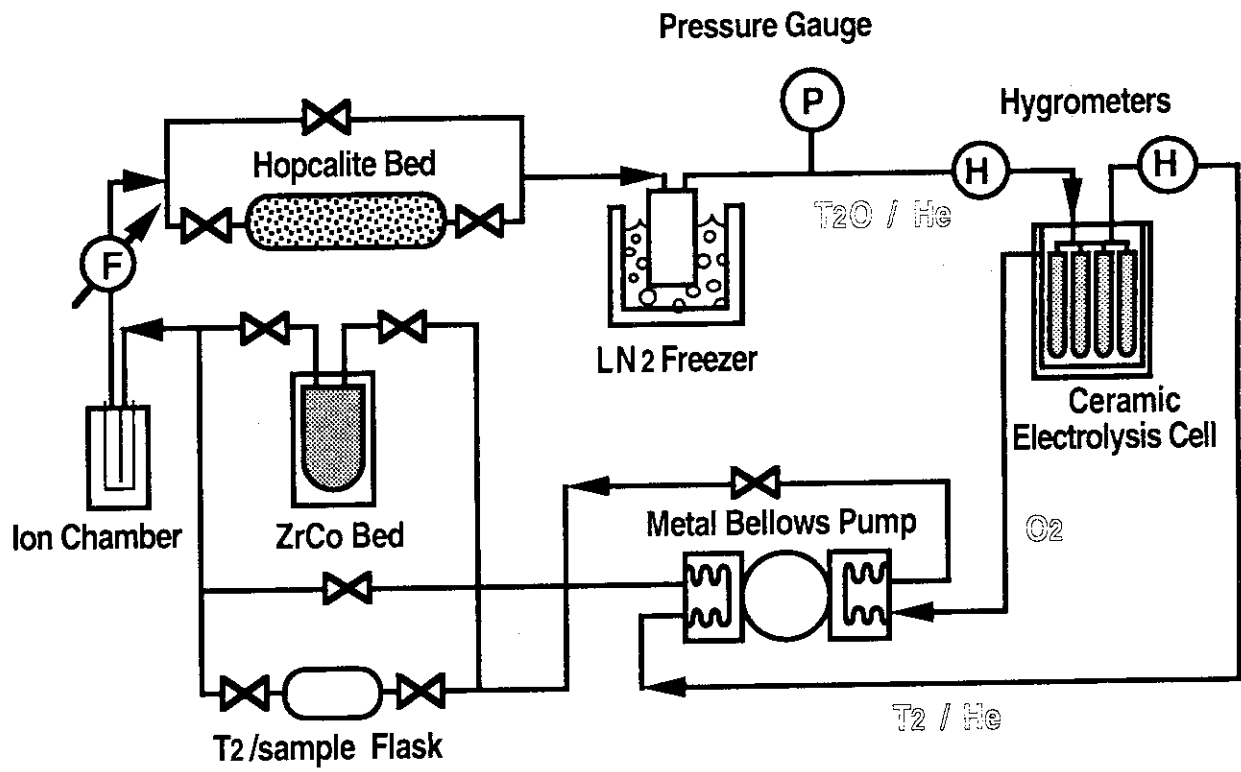
Fig. 3. Schematic of the ceramic electrolysis cell.

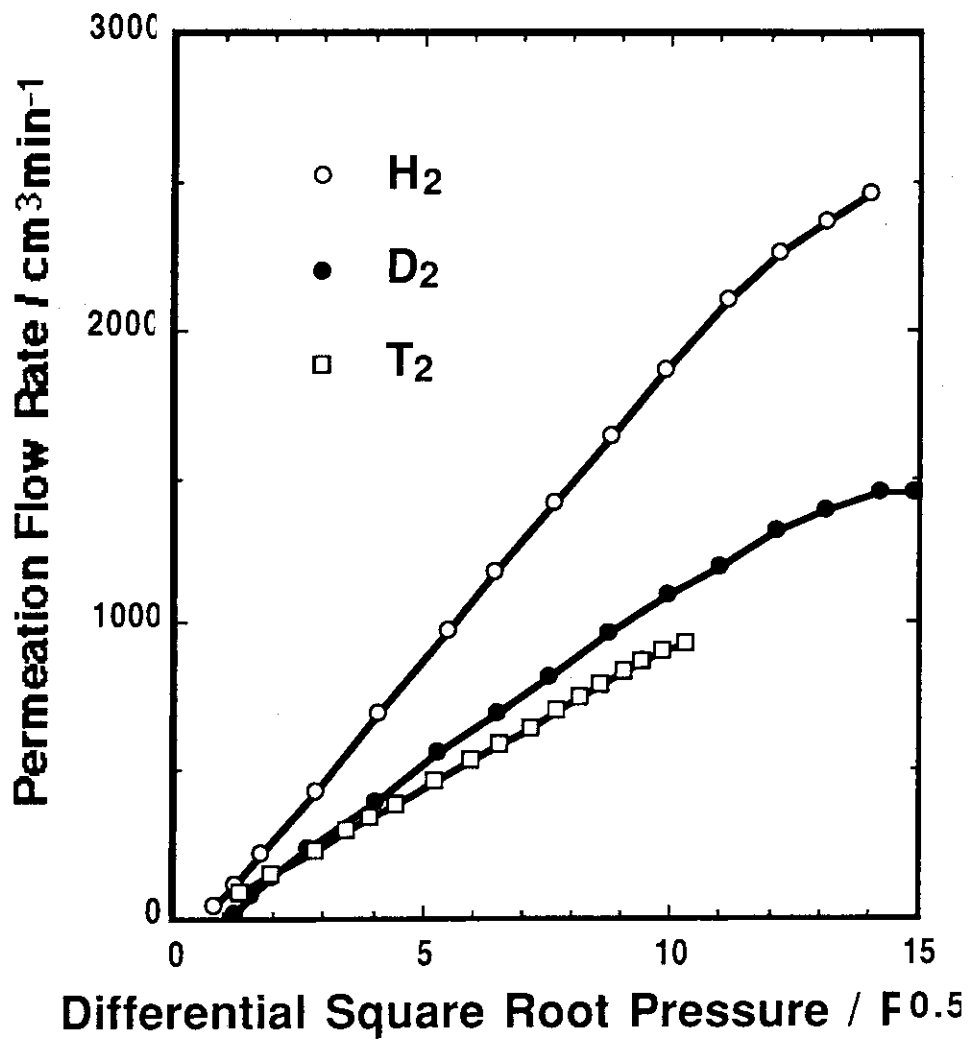Fig. 4. Flow diagram of the CEC experiments.

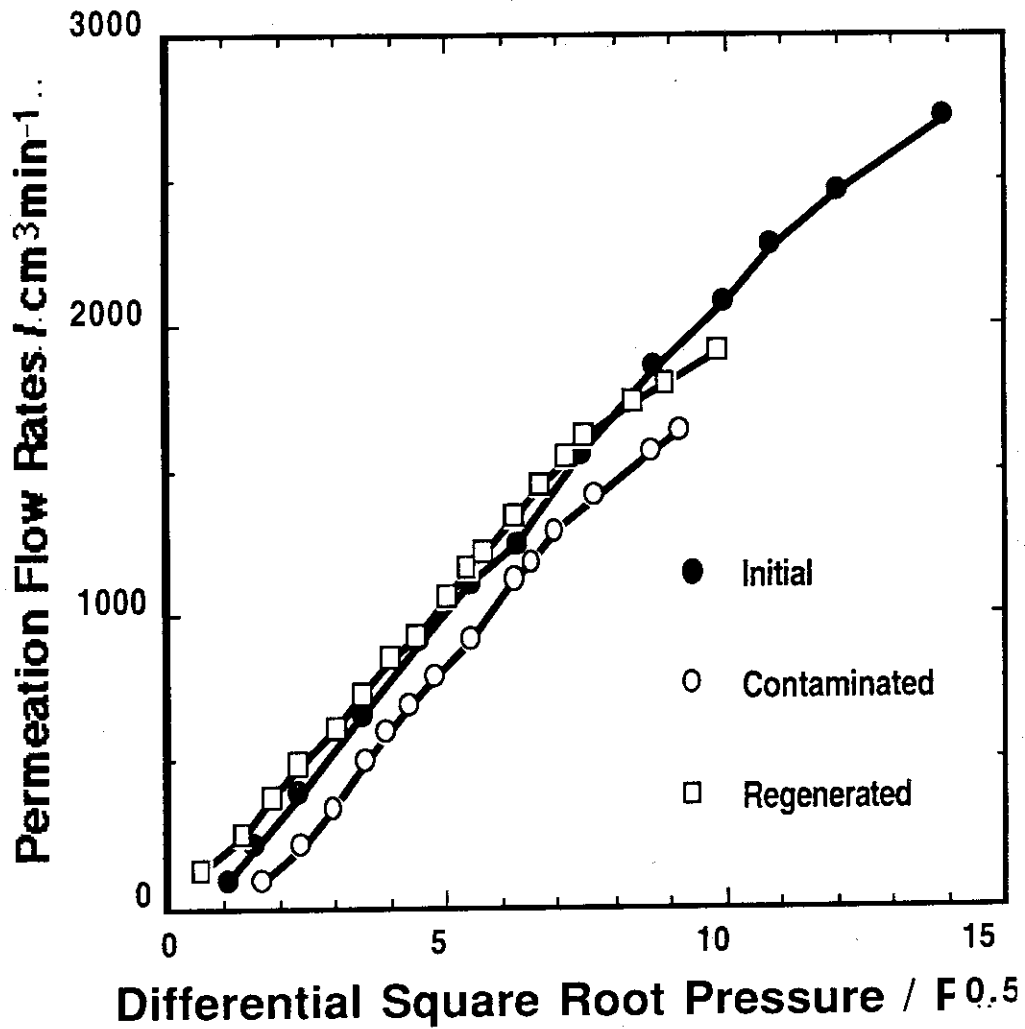Fig. 5. Permeability of pure hydrogen isotopes through the diffuser.

Fig. 6. Regeneration of the diffuser after long-term exposure to T_2-CO. Permeability of hydrogen (H_2) was measured before and after the exposure to T_2-CO , and after the oxidation followed by reduction.
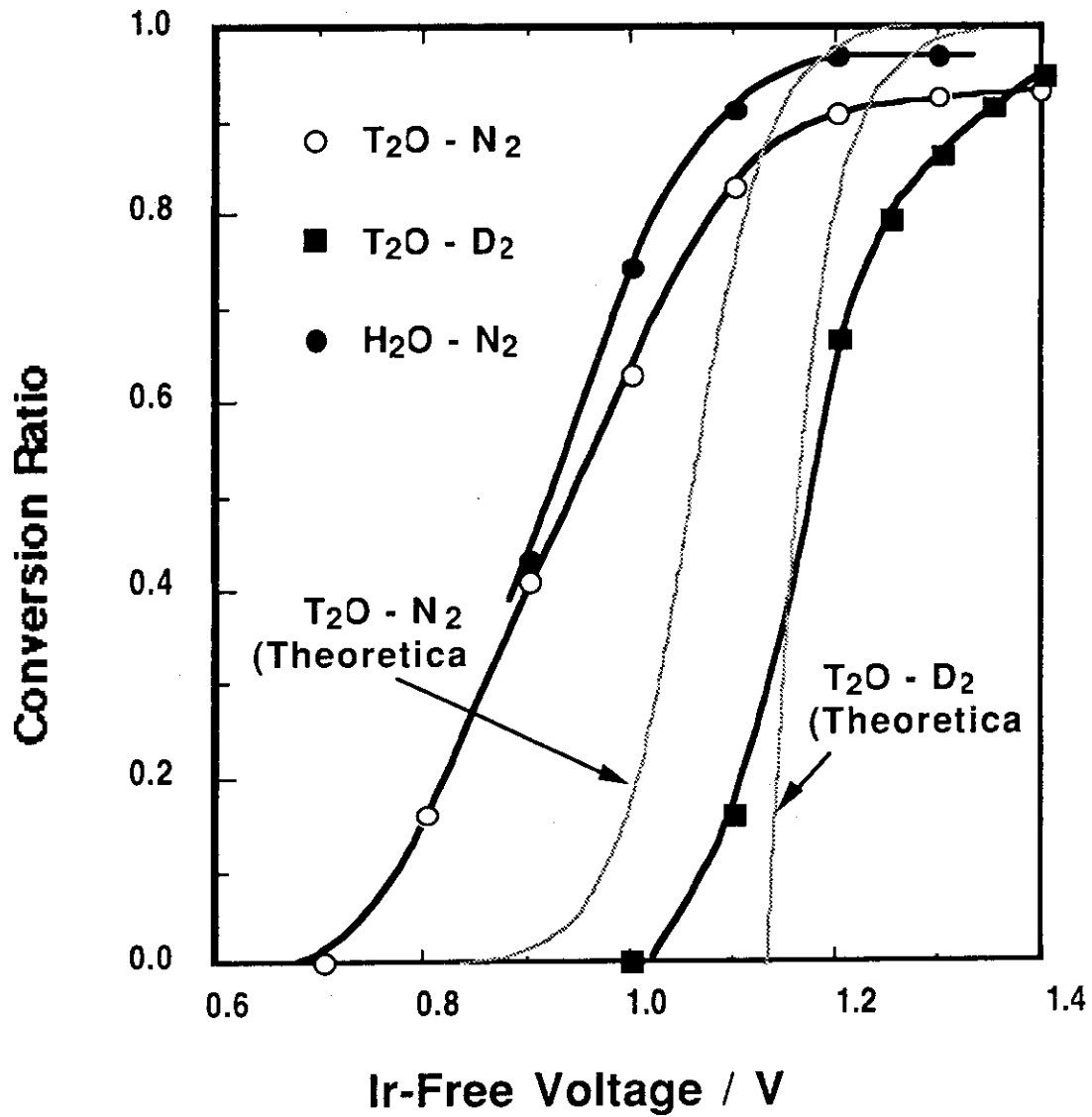
Fig. 7. Conversion efficiency from vapor to hydrogen for H_2O-N_2, T_2O-N_2, and T_2O-D_2 systems at the electrolysis cell. Theoretical relation is also shown.
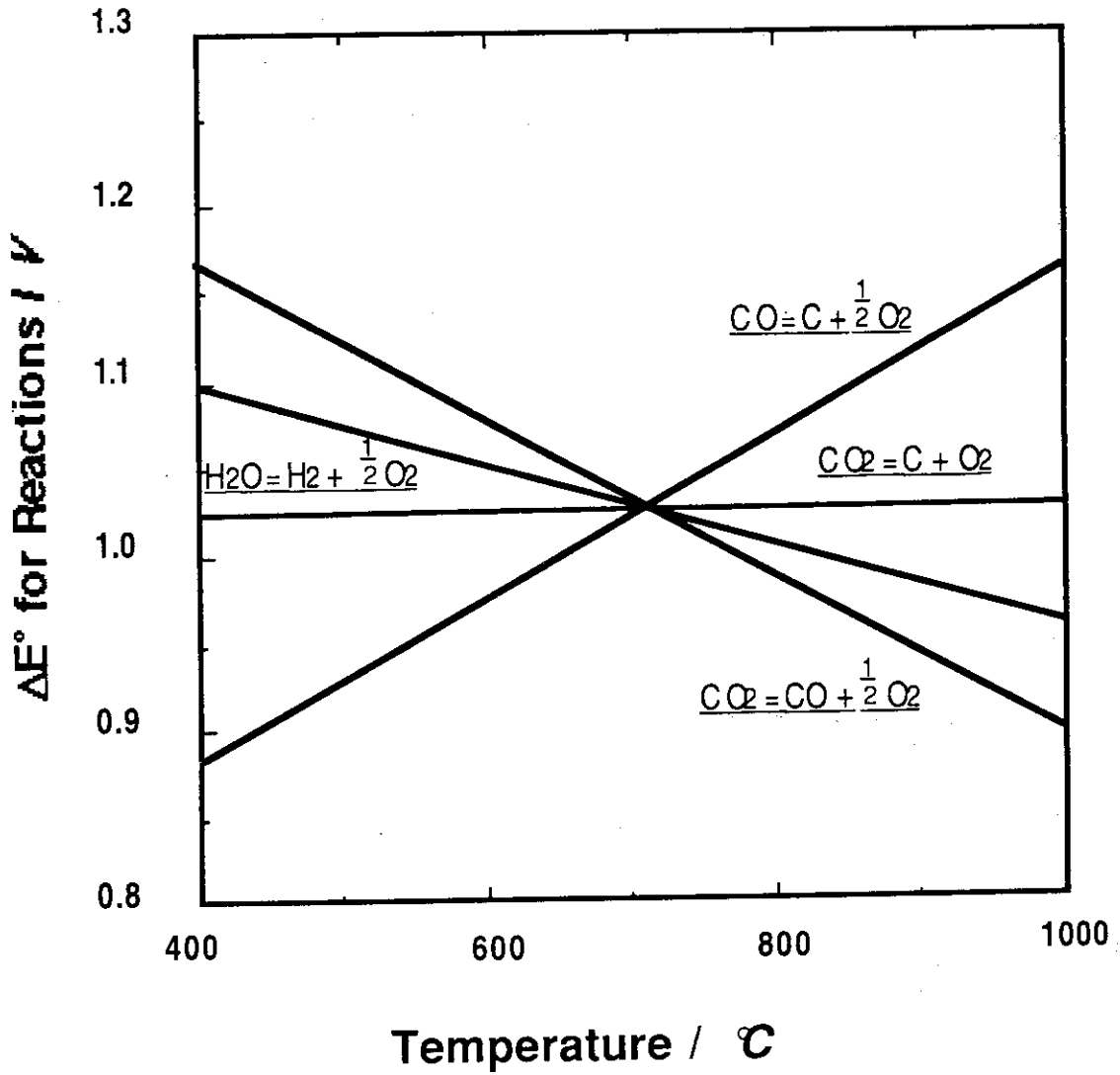
Fig. 8. Temperature dependence of the electrochemical potentials for equilibria of H_2O-CO_2 systems.
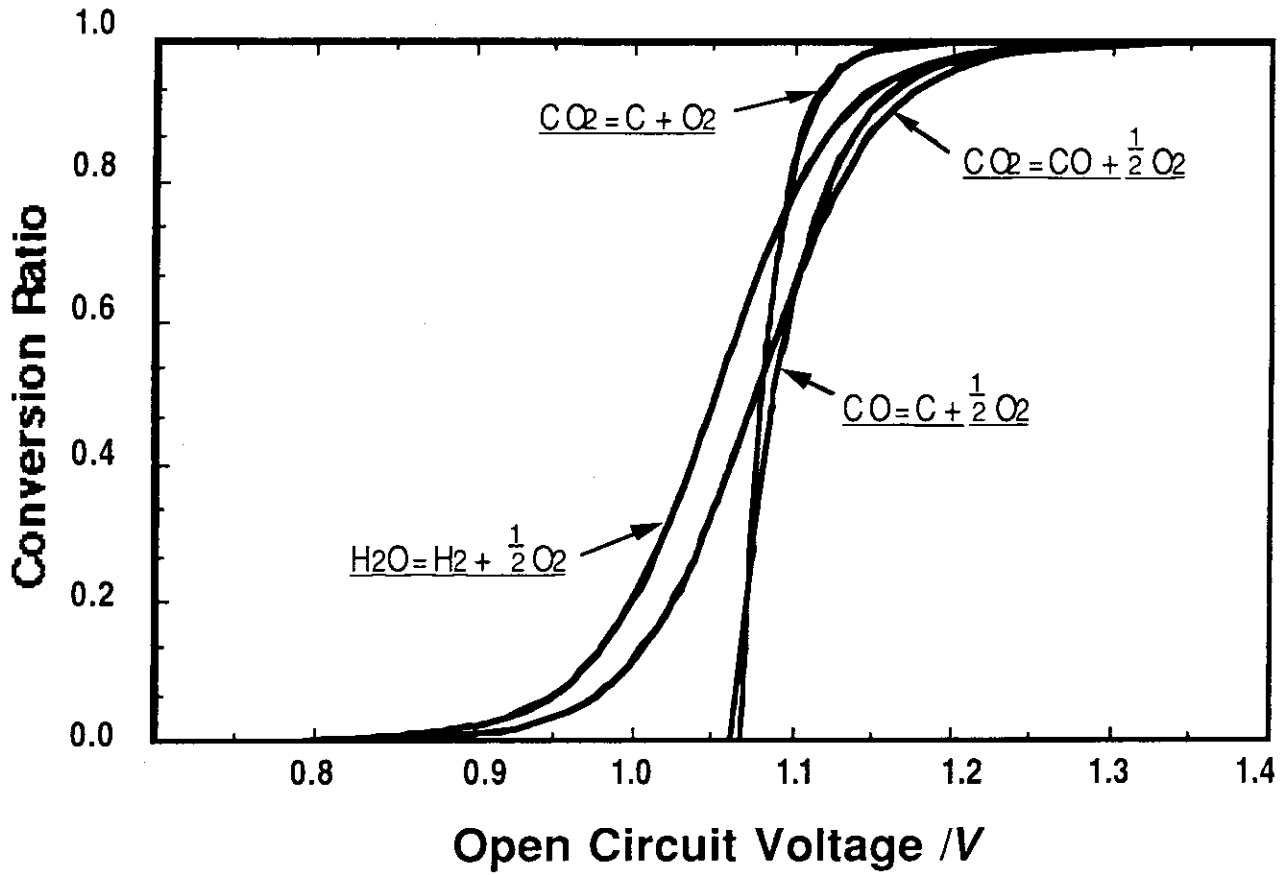
Fig. 9 Theoretical equilibrium conversion of H_2O and CO_2 at the electrolysis cell at 600°C. Feed concentration was assumed to be 0.1 for CO and CO_2.
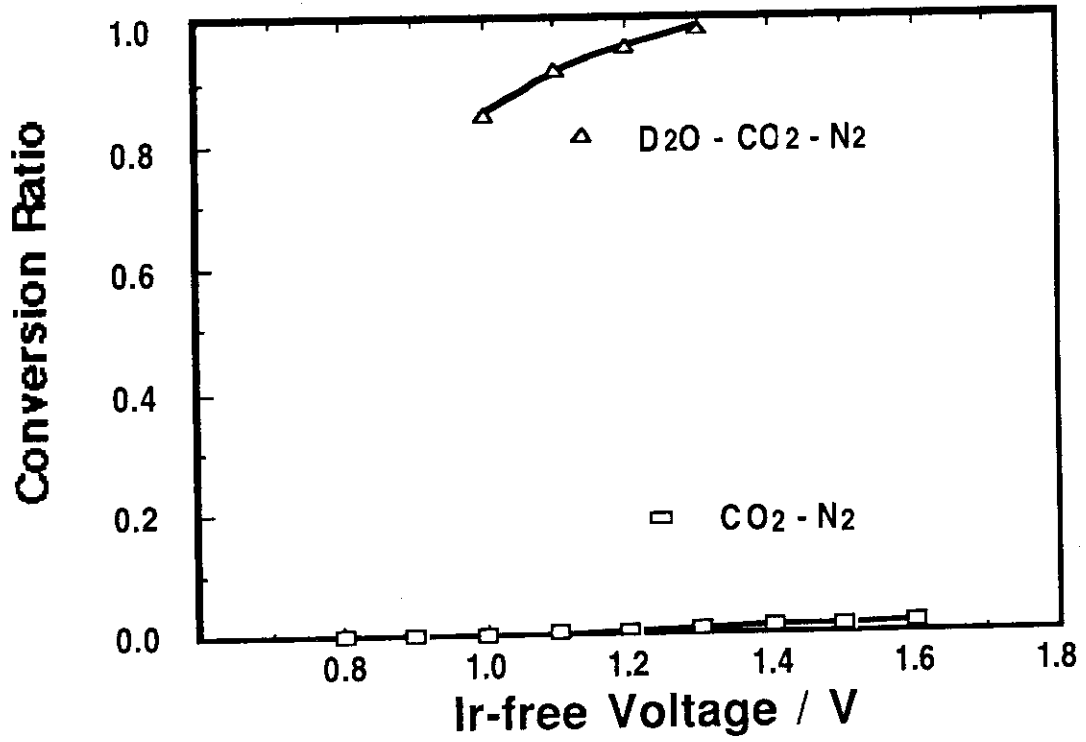
Fig. 10 Electrolysis of CO_2 - N_2 and D_2O - CO_2 - N_2 .