Reports

Hydrogen: Electrolytic Technique for Purifying It and Removing It from a Gas Stream

Abstract. *Purified hydrogen is obtained by impressing a potential gradient across a cell containing two efficient electrodes separated by a barrier electrolyte phase and passing an impure hydrogen stream into the anode compartment. Power requirements are low and can be controlled through the resistance of the electrolyte. The technique can also be used for pumping and accurate metering.*

The palladium or palladium-silver diffuser is the traditional laboratory method for purifying and removing hydrogen from a gas mixture. However, the reversible nature of the hydrogen electrode and the fact that high-current, low-polarized hydrogen electrodes are readily prepared make feasible an additional convenient technique involving the use of an electrolyte as a medium for transport of hydrogen and as a barrier to other gases. The hydrogen is selectively removed from the gas stream by adsorption and ionization at an anode to form hydrogen ions which are transported through the electrolyte under a slight potential gradient to a counter-electrode where pure hydrogen gas is reformed. This may be represented by the following steps in acid solution.

$$H_2 \longrightarrow 2H^+ + 2e \quad \text{(anode reaction)} \qquad (1)$$

$$2H^+ \text{ (anode)} \xrightarrow[\text{electrolyte}]{} 2H^+ \text{ (cathode)} \qquad (2)$$

$$2H^+ + 2e \longrightarrow H_2 \quad \text{(cathode reaction)} \qquad (3)$$

Thus hydrogen is separated from materials which are relatively insoluble in the electrolyte. When the hydrogen electrode is reversible or nearly reversible at both sides of the purification cell, little electrical power is necessary for the transport of the hydrogen. There is loss due to current-resistance drop (*IR* loss) in the electrolyte part of the cell. The Nernst relationship holds, and there is a small opposing voltage due to concentration effects when hydrogen is being removed from a dilute gas stream.

The electrolyte may be acid ion-exchange membrane, electrolyte soaked matrix (sorbent material), or liquid electrolyte bounded by ion-exchange material or porous electrodes impermeable to liquid. The electrolyte structure should be such as to minimize the passage of gaseous material.

Base electrolyte is also operable; here electrode reactions can be represented as

$$H_2 + 2OH^- \underset{\text{cathode}}{\overset{\text{anode}}{\rightleftharpoons}} 2H_2O + 2e \qquad (4)$$

The external circuit used with the hydrogen purification cell incorporates an adjustable voltage source and an ammeter in series with the cell. The current indicates the amount of hydrogen being purified. A potentiometer in parallel with the cell permits measurement of the voltage drop across the cell. On one side of the cell a stream of hydrogen and other gases may flow. On the other side a stream of purified hydrogen emerges. The cell may also be operated as a static system for the purification of a given quantity of gas.

Figure 1 is an exploded schematic diagram of the modified test cell (*1*). The assembly is held together with bolts. Electrodes are porous, and it is desirable that they have high surface area. Electric potential is applied to the electrodes through potential delivery screens which are platinum or electrolyte inert metal (*2*). Electrodes are molded catalytic metal powder—polytetrafluoroethylene unsupported or supported on metallic screen (*3*). The catalyst also may be deposited on carbon. Suitable catalytic materials are platinum, palladium, rhodium, nickel, and other metals used in hydrogen electrodes.

Sealing gaskets are of rubbery material and in the present cell permit exposure of 4.9 cm^2 of electrode surface. The rubber used depends on the electrolyte composition and the temperature of operation of the cell. At high current densities, the hydrogen purification cell heats up and potential requirements decrease.

The inlet gas stream is saturated with water vapor as is the purified hydrogen. Mass spectrometric analyses of the purified hydrogen generally show purities greater than 98 percent, and substantially pure hydrogen should be produced with suitable electrolyte barriers.

Table 1. Performance data for hydrogen purification cell at 25°C.

Electrolyte	Initial cell resistance (ohm)	Voltage drop at given current		Inlet gas
		volt	amp	
Pd electrodes (11.2 mg/cm²) on stainless-steel screen				
5 disks filter paper saturated with 6*N* H_2SO_4	0.24	0.09	0.3	H_2
		0.29	1	H_2
		0.30	1	40% H_2, 60% N_2
Pt electrodes (11.2 mg/cm²) on stainless-steel screen				
5 disks filter paper saturated with 6*N* H_2SO_4	0.22	0.41	1.7	H_2
		0.99	0.3	Manufacturer's gas*
Zerolit C20 cation ion-exchange membrane	0.49	0.18	0.3	H_2
Aqueous 23% KOH on 5 disks filter paper	0.41	0.15	0.2	H_2
		0.19	0.2	40% H_2, 60% N_2
Gelman (SA) membrane† with 6*N* H_2SO_4	0.18	0.34	1.8	H_2
		0.29	1.5	40% H_2, 60% N_2
Rh electrodes (7 mg/cm²)				
5 disks filter paper saturated with 6*N* H_2SO_4	0.24	0.26	0.5	H_2
Pt electrodes (9 mg/cm²) on tantalum screen				
5 disks filter paper with 2*N* $HClO_4$	0.23	0.54	2.1	H_2

* Matheson Co., 24% CH_4, 3% C_2H_6, 18% CO, 55% H_2. † Gelman Instrument Co., Chelsea, Mich.

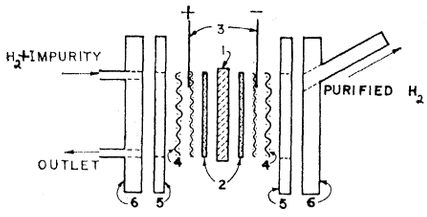

Fig. 1. Exploded section of model hydrogen purification cell: 1, saturated filter paper or membrane; 2, electrodes; 3, potential delivery screens; 4, spacers; 5, gaskets; 6, plastic casing.

Some typical performance data are given in Table 1. The hydrogen purification cell performs quite satisfactorily over a variety of conditions. Two amperes per minute is equivalent to about 15 cm^3 of hydrogen gas per minute. If speed of purification is important, electrode area and membrane resistance as well as temperature are readily altered. The calculated rate of purification was equal to the observed rate on the basis of coulombs passed through the cell. The results with Manufacturer's gas, containing carbon monoxide, indicate some poisoning of the hydrogen electrode. It is desirable to minimize the concentration of such gases in the impure gas stream or to use poison-resistant electrode catalysts.

Results with nitrogen-hydrogen mixtures are of interest since they suggest the catalytic decomposition of ammonia as a source of hydrogen. Since several hydrogen purification cells can be connected in series or in parallel, the purification process itself can be self-powered by using some hydrogen in a hydrogen-oxygen fuel cell. The purification cell also provides a means of pumping and providing hydrogen in accurate quantities when controlled atmospheres are desired. The cell may also be used as a large-scale chemical processing tool.

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References and Notes

1. G. V. Elmore and H. A. Tanner, *J. Electrochem. Soc.* **108**, 69 (1961); L. W. Niedrach, *ibid.* **109**, 1092 (1962).
2. When the electrodes are good conductors, potential may be applied directly at the electrode. When potential delivery screens are used with fragile electrodes, it may be necessary to use spacers of inert metal to press the delivery screens against the catalytic electrodes.
3. W. T. Grubb, "Proc. 16th Ann. Power Sources Conf." (PSC Publications Committee, P.O. Box 891, Red Bank, N.J.), pp. 31–34.

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Xanthine Dehydrogenase in Drosophila: Detection of Isozymes

Abstract. *Two or possibly three isozymes of the enzyme, xanthine dehydrogenase, have been detected in wild-type* Drosophila melanogaster *by starch-gel electrophoresis. Two genes, rosy and maroon-like, may control these isozymes by producing two different polypeptides that assemble in groups of three or four.*

Much evidence for the existence of enzymes in multiple molecular forms, or isozymes, has recently been accumulated (*1*). Studies of the genetic control of isozyme formation have been limited, however, by the fact that in the most well-known isozyme system, lactate dehydrogenase (LDH), only one mutant has been found among various laboratory mammals (*2*). Nevertheless, it has recently been postulated that the five electrophoretically distinct isozymes of LDH are controlled by two genes (*3*). Now it is known that at least two genes are involved in the synthesis of a different enzyme, xanthine dehydrogenase (XDH) in *Drosophila:* the rosy gene (*ry*) on the third chromosome, and the maroon-like gene (*ma-l*) on the X-chromosome (*4*). It seemed worthwhile, therefore, to determine whether isozymic forms of this enzyme exist; indications that such forms may occur were reported recently in an independent study by Keller *et al.* (*5*).

Adult wild-type *Drosophila melanogaster* (Oregon-R) were homogenized in 0.05*M* tris-buffer (*6*), *p*H 8, at a concentration of 40 mg of flies per milliliter. Norite-A was stirred in (40 mg/ml), and the mixture was allowed to stand for 30 minutes. The supernatant of this mixture, after a twofold centrifugation (30,000*g*, 30 minutes each) was subjected to electrophoresis in a starch gel made up in 0.05*M* tris-buffer, *p*H 8.7; 0.25*M* tris was used as the electrode buffer. A starch paste containing 100 to 150 μl of enzyme preparation was inserted into a slit in the gel. All these operations were performed below 5°C. Electrophoresis was continued, in the cold, for 8 hours at a voltage drop of 6 volt/cm, after which the starch gels were treated in three ways:

1) Gels were cut into 1 mm wide sections parallel to the origin. Each section was incubated in a separate test tube on a shaker in the dark at 23°C for 8 to 12 hours in an assay mixture containing tris-buffer (0.05*M*, *p*H 8, 0.4 ml), NAD (*7*) (10^{-3}*M*, 0.02 ml), and 2-amino-4-hydroxypteridine (*8*) (10^{-3}*M*, 0.02 ml). After incubation, the mixtures were centrifuged for 30 minutes at 30,000*g*, and the supernatants were placed in a Turner fluorometer, model 111, equipped with a 360 mμ primary and 405 mμ secondary filter, so that the fluorescence of the product, isoxanthopterin, could be measured.

2) A 50-μl aliquot of each of the above supernatants from each tube was applied to chromatography paper (Whatman No. 1) and subjected to ascending chromatography in the dark, in a solvent made of propanol and 1-percent ammonia in the ratio 2 : 1 (*9*). Isoxanthopterin was detected by its fluorescence and R_F by means of an ultraviolet light source emitting primarily at 360 mμ; the amount of fluorescence was estimated by eye.

3) Gels were also cut into horizontal strips, which were then incubated for 8 hours at room temperature in a histological staining mixture similar to the one used for detection of LDH isozymes (*10*), containing a saturated solution of hypoxanthine (9 ml), NAD (*7*) (10 mg/ml, 2 ml), phenazine methosulfate (1.6 mg/ml, 5 ml), nitro blue tetrazolium (*11*) (1 mg/ml, 5 ml), and tris buffer (0.2*M*, *p*H 8, 45 ml). Purple bands of formazan precipitate indicated the sites of activity of xanthine dehydrogenase in the starch.

The results in Fig. 1 show that the entire activity moved toward the anode. The graphs obtained by both the fluorometer and chromatography techniques indicate that within the first 90 mm

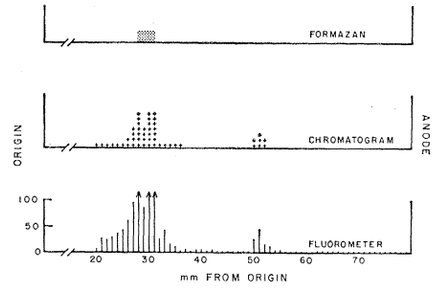

Fig. 1. Representative zymograms of xanthine dehydrogenase from wild-type *Drosophila,* obtained by three different methods as explained in the text. The number of + symbols in the middle graph reflects the estimated intensity of fluorescence. The scale on the ordinate of the lowest graph represents arbitrary units of fluorescence; arrows indicate fluorescence values exceeding the scale.