USING RADIOTRACERS TO STUDY HYDROCARBON ADSORPTION DIRECTLY AT ELECTRODES

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INTRODUCTION

Recent research on low-temperature hydrocarbon fuel cells has revealed the importance of the role of adsorption in various electrode processes. Knowledge of the concentration and composition of adsorbed reactants, products, or intermediates on the electrodes and in the electrolyte is needed for a better understanding of such processes as electroreduction, electrooxidation, and formation of intermediates.

Programmed potential electrochemical techniques (1-3) have yielded some information about reactant adsorption by inference from oxidative stripping of the electrode, but no adequate techniques have been available to permit direct measurements while the cell is operating. However, the fact that radiolabeled organic molecules have been used successfully to detect adsorbed films on solid surfaces (4,5) has lead to several studies of the use of radiotracer techniques for measuring electrode reactions. For example, workers at the University of Pennsylvania have used a thin, gold foil as an electrode and have counted activity through the foil (6), or have used a movable metal tape which is withdrawn from solution and counted (7,8). Such techniques have permitted studies of the adsorption behavior of some aromatics (9,10), olefins (11), and amines (6,7) on several metals. Nevertheless, the thickness of the metal foils limits the sensitivity of the former measurements, and the necessity of withdrawing the tapes prevents continuous samplings in the latter method.

To avoid these shortcomings, we have adapted a method that was developed by Cook (4) and later modified by Walker and Ries (5). In our adaption, a metal film, deposited directly on a mica substrate, is made the electrode in a fuel cell, and the activity of a radiolabeled hydrocarbon is counted directly through the mica while the cell is operating. High sensitivity is possible because the metal film is only a few thousand angstrom units thick, and the very thin mica sheet absorbs little radiation compared with metals.

We have solved the major design problems associated with the technique. We have been able to produce stable, reusable, thin-film electrodes that are thin enough to allow high sensitivity in counting but thick enough to behave as equipotential electrodes. The cell is small enough to conserve the radiolabeled hydrocarbon, but is easy to fill and empty and is free of components that would adsorb fuel from the electrolyte. Air is excluded rigorously, and operation is confined to low temperatures to keep adsorption and oxidation rates low enough to be studied with 30-second counting periods.

This paper describes the design and operation of the cell and summarizes our studies of the adsorption and oxidation of various concentrations of radiolabeled n-butane at platinum electrodes in a sulfuric acid electrolyte at 25°C.

EQUIPMENT AND PROCEDURE

Apparatus

The adsorption cell and its associated electrodes are designed to minimize mixing of the anode and cathode products during electrolysis. As shown in Figure 1, the cell body is a shallow, 7-cc, glass cup, about 5 cm in diameter, to which two sidearms are attached. One sidearm is drawn to a fine tip within the cell (to serve as a Luggin capillary) and is equipped with a tapered joint to which an autogenous hydrogen reference electrode (12) is attached during electrolysis. The tapered joint is also used for attachment of a syringe by which the cell is filled or emptied. The other sidearm contains the platinum gauze electrode that serves as a cathode. The contents of the cell are magnetically stirred at 100 rpm.

The thin-film electrode, which serves as an anode, is mounted vertically to prevent accumulation of gas bubbles on its surface. It comprises a 2000-Å layer of platinum, bonded to a mica support by means of a 100- to 200-Å layer of tantalum on tantalum oxide. It is prepared as follows: A mounted piece of India Ruby Mica (Spruce Pine Co.), about 6 mils thick and 4.3 cm in diameter, is degreased in benzene, cleaned in chromate cleaning solution, mounted in a conventional sputtering apparatus (13), and evacuated overnight at 4×10^{-3} Torr. Then tantalum is reactively sputtered onto the mica in dry air at 0.05 Torr and 2200 volts at 10 ma for 7 minutes. The resultant layer is purged with oxygen-free argon, and the tantalum sputtering is continued in argon for 20 minutes. Finally, platinum is sputtered onto the tantalum in argon at 0.05 Torr and 1025 volts at 5 ma for 32 minutes.

Before the electrode is sputtered, the mica substrate is mounted between two metal rings, one of platinum and the other of Unalloy 50 (Fe-Ni), as shown in Figure 2. The rings are cemented to the mica with Pyroceram Number 95, vitrified at 450°C. After the sputtering, the finished electrode assembly is cemented to the cell with melted polyethylene. When the electrode is in position, the area of platinum exposed to the electrolyte is 15.94 cm^2, and the area of mica exposed to the counter is 11.33 cm^2. Measured from edge to center, the electrode has a resistance of about 1 ohm.

The counting equipment comprises a proportional counter (Model D-47, Nuclear Chicago Corp.) employing P-10 feed gas, and a transistorized scaler (Radiation Instrument Development Laboratories) with a print-out.

The potential of the thin-film electrode is controlled by a Brinkman Model 61-R fast-rise potentiostat in a conventional circuit. A galvanostat consisting of a helipot and a 90-volt battery is used for constant-current anodic or cathodic stripping. Potential during stripping is recorded on a 10-mv Brown recorder through a Keithly Model 610 electrometer.

Materials

The radiolabeled n-butane was obtained from the New England Nuclear Corporation. It had a C^{14} activity level of 1.9 millicuries per millimole and was used without further purification.

The sulfuric acid was J. T. Baker reagent grade.

Water for dilution was laboratory distilled water that had been redistilled twice from quartz into quartz receivers. It was deaerated by evacuation.

Stock solutions of butane were stored over mercury and transferred by displacement with mercury to prevent contact with air. All other reagents and solutions were deaerated before mixing, and transferred under purified argon.

The argon was purified by passage over copper turnings at 800°C.

Procedures

Preparation of Test Solution. Test solutions containing various concentrations of radiolabeled n-butane in 1N H_2SO_4 were prepared by diluting aliquots of the butane stock solution with oxygen-free electrolyte and oxygen-free, double-distilled water.

Counting Rate Calibration. Counting rates were calibrated against a standard source of known activity, and all data were corrected for attentuation of activity through the mounted thin-film electrode and for background and solution counts. Reported count rates represent true values at the electrode surface.

Determination of Electrode Area. To determine the actual surface area of the thin-film electrode, the surface was potentiostated at 1.2 volts in 1N H_2SO_4 for 3 minutes. Then the oxide was stripped galvanostatically at 2 ma (125 $\mu a/cm^2$). A sharp potential arrect was observed. The true area was calculated from the total number of coulombs required to strip the oxide. A factor of 0.3 millicoulombs/cm^2 derived from other work (14) was used.

Adsorption Measurements. In a typical adsorption run, the cell was filled with a blank 1N H_2SO_4 solution that contained no n-butane, and the thin-film electrode was pretreated (reduced) at 0.1 volt. Then the blank solution was replaced with the test solution, and the potential was controlled at one or more predetermined voltages while the adsorption at the thin-film electrode was measured in counts per minute per cm^2 of true electrode area. The reference electrode was operated at 5 ma/cm^2 in the same electrolyte (1N H_2SO_4).

RESULTS AND DISCUSSION

In the initial experiments, the adsorption of radion-n-butane in 1N H_2SO_4 at 25°C was studied as a function of time, electrode potential, and n-butane concentration. For a particular concentration of n-butane, electrolysis was started at 0.1 volt and adsorption was measured until an equilibrium value was reached. Then voltage was increased by 50 to 100 mv, and equilibrium adsorption was again noted. This procedure was repeated from 0.1 to 0.5 volt with 5×10^{-4} and 5×10^{-5} molal n-butane. For the latter solution, the voltage was then decreased in several increments.

As shown in Figure 3, equilibrium adsorption was negligible below 0.2 volt, showed a maximum at 0.3 volt, regardless of n-butane concentration, and again was negligible above 0.5 volt. However, when the voltage was decreased, less n-butane was readsorbed at 0.3 volt and more was retained at 0.1 volt.

Other workers (7,10) have found that the potential at which maximum adsorption of n-decyl amine and naphthalene occurs varies with concentration. They attribute this concentration dependence to variations in the electronic interactions of the pi electron system of the adsorbed molecules with the platinum. The fact that we observed no such concentration dependence may reflect a lack of electronic interaction between n-butane and the electrode.

Galvanostatic data show that at least part of the butane first adsorbed at 0.3 volt is displaced by hydrogen atoms adsorbed when the potential is switched to 0.1 volt. Anodic potential sweep data suggest that the butane adsorbed at 0.3 volt occupies sites normally involved in the second hydrogen wave ($\sim$0.35 volt) usually seen in potential sweep scans. The decrease in adsorption at higher voltages occurs because oxidation of n-butane begins to compete with adsorption above 0.3 volt. The subsequent change in the level of adsorption as the voltage was decreased indicates that an irreversible reaction occurs on the electrode above about 0.3 volt. For example, Figure 4 shows how the adsorption-time behavior of n-butane is affected by a change in potential. Here, equilibrium adsorption was established at 0.1 volt, and then the potential was increased 0.3 volt for several hours. When the potential was decreased to 0.1 volt, some of the n-butane was desorbed, but the equilibrium concentration retained on the electrode was much higher than the value measured initially at 0.1 volt.

Examination of the electrode as the potential was cycled repeatedly between 0.1 and 0.3 volt showed that such adsorption-desorption hysteresis is caused by the formation of a residue on the platinum. The residue forms slowly, will not hydrogenate off of the electrode at 0.1 volt, and will not wash off in blank electrolyte. However, it can be removed completely by oxidation at 1.2 volts.

In an effort to quantify the surface concentration of this residue, we first measured the maximum adsorption of n-butane as a function of concentration at 0.3 volt. Then we measured the amount of residue formed at each concentration as a result of repeated recycling between 0.1 and 0.3 volt. Based on the true surface area determined for the electrode, we were thus able to calculate the saturation adsorption of n-butane at 0.3 volt and relate it to the amount of surface covered by the residue. The concentration isotherms and the surface coverage data are shown in Figure 5 and Table I.

Results of the galvanostatic procedure used to measure the residues are illustrated in Figure 6. The residue-covered electrode was first potentiostated at 0.3 volt. The residue was then removed by oxidation at 63μ a/cm^2, while the number of coulombs passed and the amount of C^{14} on the window were recorded simultaneously, starting at 0.3 volt and terminating at 1.2 volts. A blank galvanostatic curve in 1N H_2SO_4 was obtained to correct for coulombic contributions from double-layer charging and from oxidation of the platinum surface. Coulometric results were also normalized to the window area by using the ratio of window area (11.33 cm^2) to total area exposed to the electrolyte (15.94 cm^2). As the residue is oxidized, the C^{14} leaves the window presumably as $C^{14}O_2$, and the count rate drops.

In Figure 6, count rate and total coulombs passed are plotted vs. potential. Oxidation of the residue begins above 0.65 volt as reflected in both curves. The initial negative values represent oxidation of hydrogen that was present on the electrode in the blank electrolyte at 0.3 volt but was not present on the residue-covered electrode. Some of the residue was much harder to oxidize and a little still remained at 1.2 volts in the scan. (The remainder can be oxidized if the potential is held constant for a time at 1.2 volts.)

As shown in Table I, if we assume that the n-butane molecules lie flat and occupy 29 Å^2, saturation is approached at a fractional coverage, θ, of 0.39. Whereas, if we take the value of 50 Å^2/molecule commonly assumed in gas phase adsorption work where imperfect packing is concluded to occur, we find that θ is 0.98. In this work the actual area occupied by butane must be taken into account because the remaining free surface area is available to other solution species. Our data show that the amount of residue varies with the concentration and accounts for about 1/4 of the initial maximum amount of n-butane adsorbed at 0.3 volt. From the data for peak adsorption at 0.3 volt vs. concentration, an equilibrium constant calculated for the adsorption (7) gives $K_{eq} = 4.85 \times 10^{-4}$. The corresponding free energy of adsorption, ΔFa, is 3 kcal/mole.

In our data for the oxidation of the residue, the count rate is directly related to the number of butane molecules originally adsorbed on the electrode. If these molecules were still intact they would yield 26 electrons each. The actual coulombic yields varied with the potential and reflected various states of oxidation of those portions of the residue removed with a given charge increment. In Figure 7, the number of millicoulombs measured is plotted against percent C^{14} removed. The curve appears to have four linear segments. On the basis of the count rate, the known specific activity, and 26 electrons per butane residue, 30 millicoulombs would be measured, and the average theoretical slope shown would be followed. The first two linear segments (45% C^{14} removal) have steeper slopes, reflecting partial oxidation of a substantial amount of the other 55% of butane-equivalent residue. The remaining 55% C^{14} is removed at a slope equivalent to one-half or less of the 26 electron slope, showing clearly the existence of an oxidized intermediate that is difficult to oxidize further. A total of 37 millicoulombs were passed in removing 80% of the residue.

CONCLUSION

The existence of the residue is interesting because previous (unpublished) work with various pulse techniques has shown that at higher temperatures there is a time-decay in oxidation rate which could result from decay of active sites, reduction of minor amounts of surface oxide (resulting from pretreatment techniques), or the formation of a residue which blocks catalyst sites. Our radiotracer data strongly support the latter. Additional experiments with stripping the residue have shown similar high initial and low final stripping rates. The partially oxidized material might be an unsaturated coke having a C/H ratio of about 1, perhaps similar to benzene. However, partially oxygenated species could also account for the observed state of oxidation. Assignment of an exact structure is not possible with the radiotracer method alone. Examination of residues from other fuel molecules, modification of the radiotracer technique to permit simultaneous C^{14} and H^3 measurement, or development of a spectroscopic method for examining the residue would be aids in that direction. Knowledge of the state of oxidation of the residue and its response to various treatments would be helpful for an understanding of the process of anodic oxidation of hydrocarbons at platinum. The radiotracer method can supplement conventional electrochemical measurements in that regard.

The radiotracer method should be used to study a number of problems in the fuel-cell area. Adsorption behavior should be studied for a variety of fuel types, such as alkanes, olefins, aromatics and naphthenes, and on other surfaces. Residues from oxidation of these fuel types and from reduction of radio-carbon dioxide should be examined in detail. Surface coverage and state of oxidation data for these reactants may reveal much about the structure and composition of surface species and their role in limiting the rate of the over-all process. Competitive adsorption in mixed liquid fuels should be explored, and the effect of poisons such as sulfur and arsenic on adsorption behavior should be assessed.

A general limitation exists with regard to the temperature range available for measurements. Adaptation of the cell and the counter

for use at higher temperatures is relatively easy to accomplish technically. But reaction rates for adsorption-desorption and oxidation increase with temperature. This eventually limits the method because feasible counting periods have a required minimum duration. For a given level of radio-activity, because of the irregular rate of decomposition of C^{14}, a minimum counting period is required to obtain small data scatter in repeated counts of the same source. For our work, 6 seconds produced some scatter. Appreciable increases in rates of sorption or oxidation processes would allow fewer samplings of count rate, eventually eliminating the possibility of simultaneous measurements.

In its present state of development, the method should accommodate acid and alkaline electrolytes and many non-aqueous electrolytes. A wide choice of electrode metals is possible. Mica is the preferred window material for hydrocarbons, but Mylar or Teflon may be useful with other reactants. Because the method has many potential applications, the cell structure should be chosen to suit the requirements of each system.

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TABLE I

ADSORPTION AND AREA PER MOLECULE FOR VARIOUS CONCENTRATIONS OF n-BUTANE[a]

n-Butane Concentration, Molal	Roughness Factor of Film-electrode[b]	Amount of Adsorption, C/M per cm^2 true		Fractional Coverage, θ[e]	
		Maximum[c]	Residue[d]	Maximum[c]	Residue[d]
7.1×10^{-6}	29.0	6	2	0.012	0.004
3.6×10^{-5}	26.3	58	14	0.12	0.028
7.1×10^{-5}	30.0	157	54	0.32	0.11
	30.9	153	50	0.32	0.10
2.1×10^{-4}	26.3	189	36	0.39	0.073
7.1×10^{-4}	29.0	189	27	0.39	0.054

a. All measurements at 25°C in 1N H_2SO_4 at sputtered platinum electrodes.
b. Determined by cathodic stripping of oxide.
c. Initial adsorption at 0.3 volt vs. hydrogen, 11.3 cm^2 exposed electrode.
d. Amount retained after repeated cycling at 0.1 and 0.3 volt, 11.33 cm^2 exposed electrode.
e. Assuming molecules lie flat and occupy 29A^2.

FIGURE 1

ADSORPTION CELL

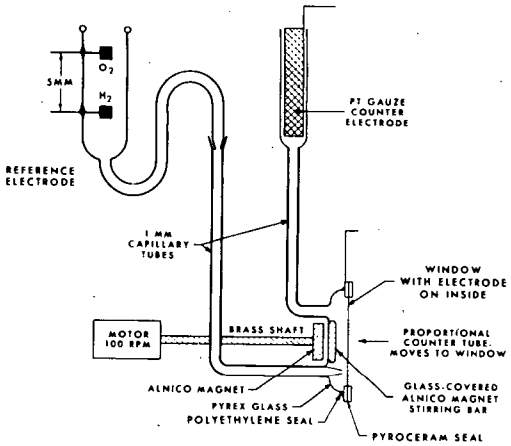


FIGURE 2

FILM-ELECTRODE MOUNTING

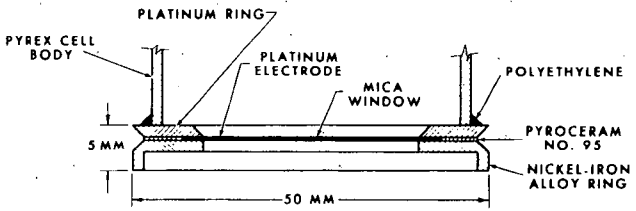


FIGURE 3

ADSORPTION OF RADIO n-BUTANE AS A FUNCTION OF POTENTIAL

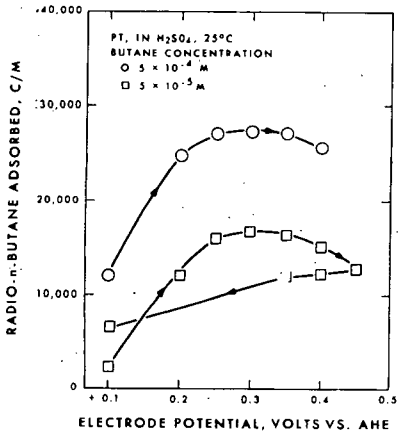


FIGURE 4

BUTANE ADSORBED VERSUS TIME AT CONTROLLED POTENTIAL

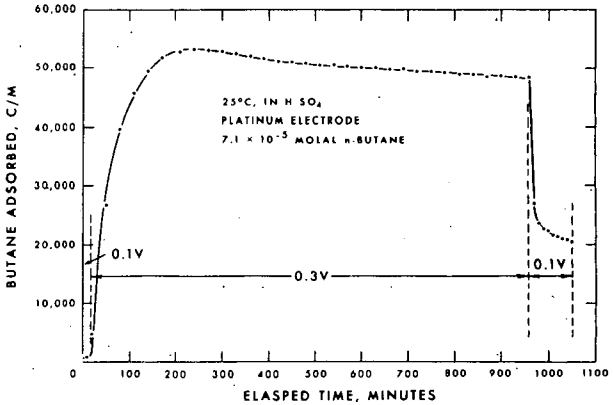


FIGURE 5

MAXIMUM ADSORPTION AT 0.3V AND RESIDUE VS. CONCENTRATION n-BUTANE

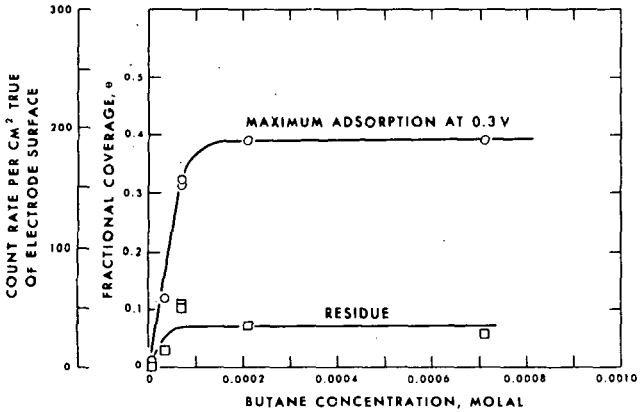


FIGURE 6

OXIDATION OF RESIDUE: SIMULTANEOUS MEASUREMENT OF AMOUNT OF ADSORBED RESIDUE AND ANODIC STRIPPING CHARGE

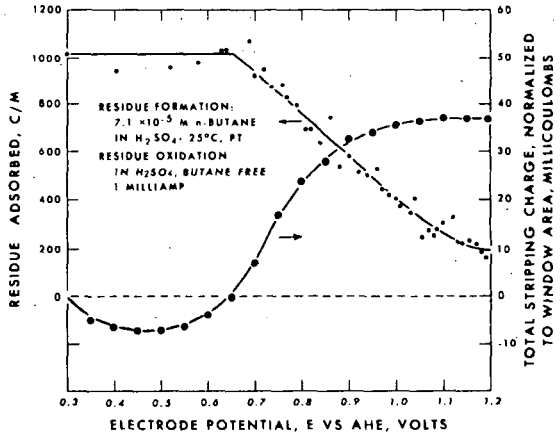
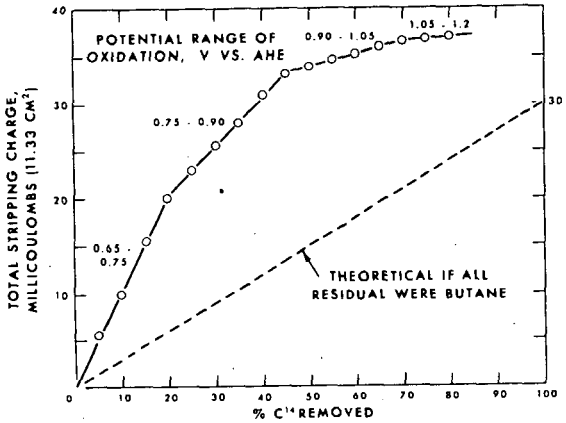


FIGURE 7

OXIDATION OF RESIDUE: ELECTRON YIELD AND POTENTIAL RANGE