

Effect of PTFE Coverage on the Performance of Gas Evolving Electrodes

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ABSTRACT

The effect of nickel electrode partial coverage with polytetrafluoroethylene (PTFE) on the electrode performance for the hydrogen evolution reaction (HER) was investigated. We show that for low current densities the only effect of the electrode coverage is to decrease the effective area. For medium current densities ($>10 \text{ mA/cm}^2$), coverage with PTFE has an overall beneficial effect in the electrode performance even with the resulting decrease in electrode surface area. Finally, for high current densities, in a regime of violent bubble release (1 A/cm^2), coverage effect is decreased but still significant.

In a gas evolving electrode, due to the magnitude of the diffusion coefficients, only a fraction of the electrode surface will interchange electrons at any given moment. This is due to partial surface coverage by bubble formation, which blocks part of the electrode surface. As a result, localized high current densities are observed on certain parts of the electrode surface. Recently, metal perforated diaphragms were partially coated with PTFE and were tested as water electrolyzer separators (1). It was shown that the PTFE coated metal is a bubble scavenger, having an overall beneficial effect on electrolyzer performance. Teflon bonded electrodes have also been used in water electrolyzers. However, it is still not clear how much, if at all, the performance of Teflon bonded porous electrodes is better than platinized or plain electrodes for gas evolution reaction and what the overall effect of PTFE on the performance of gas evolving electrodes is (2, 3).

In this work, we investigated the effect of partial electrode surface coverage with PTFE on the electrode performance for the hydrogen evolution reaction (HER).

Experimental

Circular stainless steel plates with an area of 10 cm^2 and 1 mm thick were initially plated in a Watts solution at 80°C . The plated sample was rotated about its axis at a constant speed in order to smooth out local electric field differences. All samples were prepared from the same stainless steel plate. The plate was initially washed in a detergent solution, mechanically scrubbed, and then cleaned in the following sequence (4): (i) degreasing in methanol for 15 min; (ii) washing in an alkaline bath (KOH 10%) for 5s; (iii) rinsing in distilled water; (iv) washing in an acid bath (H_2SO_4 5%) for 5s; and (v) washing in distilled water.

The nickel-plating solution consisted of the following compounds dissolved in distilled water: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 300 g l^{-1} , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 45 g l^{-1} , and H_3BO_3 , 30 g l^{-1} . The resulting solution was stirred at 80°C in a Pyrex beaker. The counterelectrode was a nickel sheet. The solution was heated to 80°C prior to each experiment. The total nickel plating time was 12 min. The current density was approximately 10 mA/cm^2 . After plating, the plates were washed with distilled water and dried.

PTFE T30 Teflon dispersion was dialyzed against water to remove the stabilizing surfactant and diluted to ca. 1% in distilled water. The dispersion was then allowed to settle within long (ca. 60 cm) glass cylinders for 15 min, after which time the lower 10% of the cylinder contents were discarded. The dispersion was allowed to settle again, and after 1h the upper half of the cylinder contents were also discarded. To prevent excessive coagulation, 1% sodium laurylsulfate was added to the remaining dis-

persion, for storage. Prior to use, it was drained from a stored, settled dispersion and replaced by distilled water.

PTFE T30 Teflon¹ dispersion was sprayed onto the electrode surface, allowed to dry, and heated in an oven preheated to 370°C . It was left at this temperature for 15 min and cooled by direct exposure to room air. The electrode surface was then washed in an acidic solution to remove the oxides formed, and another layer of nickel was electrolytically deposited on the electrodes. The purpose of this second deposition is to give mechanical stability to the Teflon layer. A photograph of the resulting surface is shown in Fig. 1. If a second nickel layer is not deposited, due to bubble formation, most of the Teflon will be removed from the surface by adsorbing to the gas-liquid interface. Deposition of a second nickel layer prevents the release of the Teflon layer even for high current densities (1 A/cm^2). During the second deposition, the current density was the same as in the first one.

The electrolytic cell employed for current density vs. potential drop measurements was a straight-walled cylindrical Pyrex beaker with a PTFE cover machined to fit (5). The cell containing 30 weight percent (w/o) KOH electrolyte was immersed in a water bath at 80°C . The test electrode and a larger planar platinum electrode were positioned facing each other at a distance of about 4 cm. The electrodes were soldered to a copper wire, and this connection was insulated with silicone rubber. The anode was not submitted to any special treatment. A membrane was inserted between them and kept fixed by a supporting frame. Mercury-mercury oxide electrodes were used as reference electrodes. ($E_{\text{Hg}/\text{HgO}} = 43 \text{ mV/NHE}$ in 5N

¹ Obtained from E. I. du Pont de Nemours and Company.

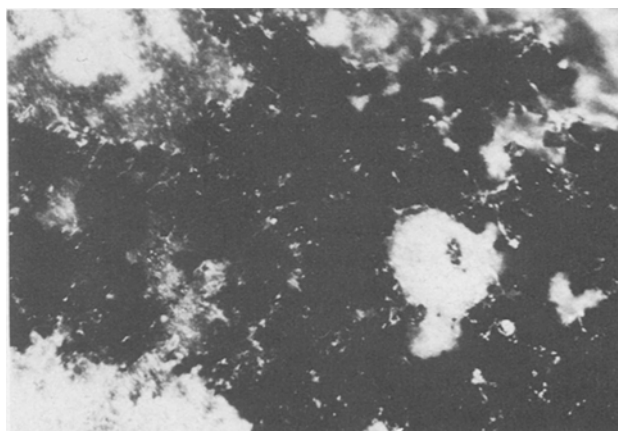


Fig. 1. Optical micrograph of a PTFE partially covered nickel surface (400 \times).

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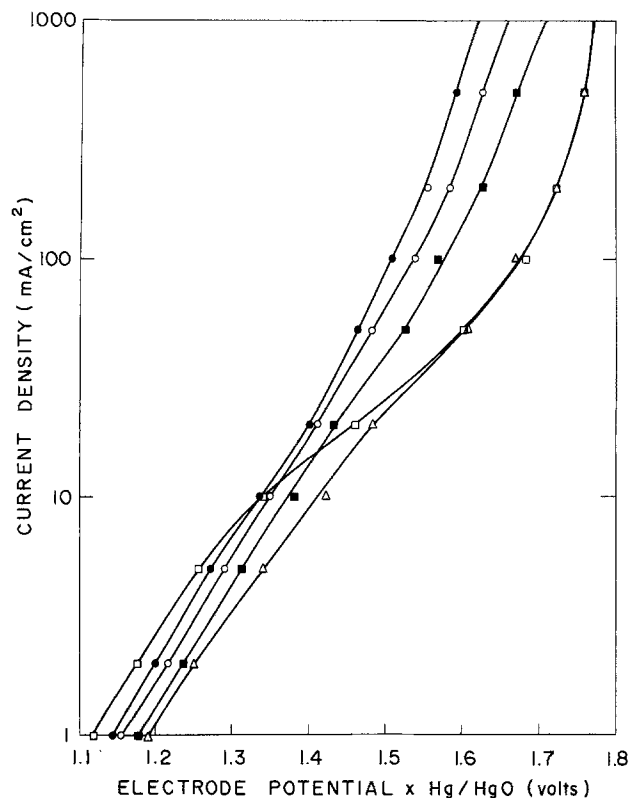
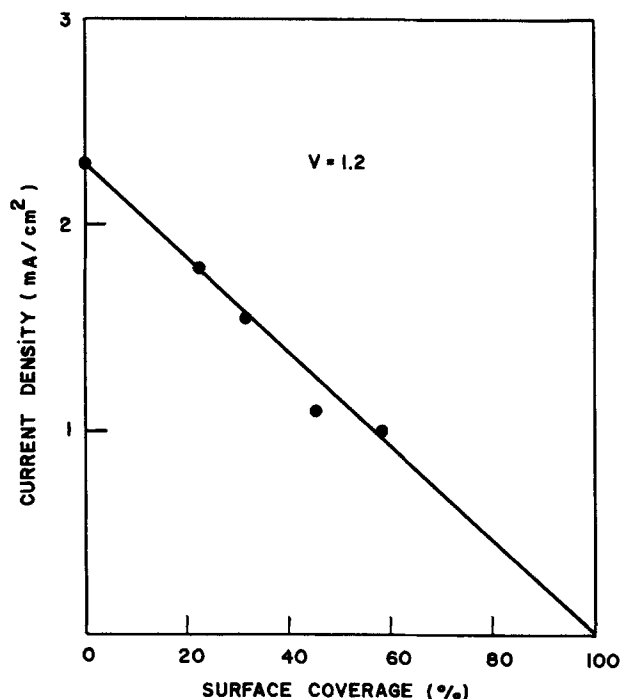


Fig. 2. Tafel plot for the H_2 evolution reaction using partial covered surface electrodes. \square : uncovered. \bullet : 20% coverage. \circ : 40% coverage. \blacksquare : 60% coverage.

KOH solution). The Hg/HgO electrode was inserted into a Luggin probe. The Luggin tip was positioned at the center of the working electrode. The characterization of the electrode was done by measuring cell voltage drop during electrolysis at different conditions, using a current interrupter technique (6) in order to obtain the IR-free electrode voltage.

Results

A number of electrodes was prepared, within surface coverage ranging from zero (uncovered) to 60%. Surfaces of the electrode samples were examined by optical mi-



croscopy. A typical micrograph is shown in Fig. 1. The irregular light (white) pattern observed corresponds to the PTFE deposit, and the dark areas are those of uncovered nickel. The picture was taken after the electrode was operated in HER regime for more than 2h at 1 A/cm². The light and dark tones indicate an irregular topography of the deposit surface. One may clearly observe that the PTFE particles are partially covered by nickel to aid their retention, mechanically. Nickel overlayers give mechanical strength to the Teflon deposits. The edge of the nickel deposit should operate very efficiently since the edges of electrodes are known to operate as efficient bubble generators. Since the metal is better wetted than PTFE, these bubbles should move from the nickel edges to the PTFE surface spontaneously.

Results of current vs. voltage measurements for the electrodes tested are shown in Fig. 2. The current densities shown in Fig. 2 are obtained by dividing the total current I by the geometric area of the circular electrodes (10 cm²). It may be seen that Teflon coverage has a significant effect on the electrode performance. Teflon coated electrodes operated at 500 mA/cm² have lower overvoltage than plain electrodes and are thus more efficient than these.

Discussion

The electrode area covered by PTFE does not participate in electron-transfer reactions, but it draws gas bubbles from the metallic sites, thus leaving more free to adsorb ions from the electrolytic solution and to reduce them. The electrode surface may be seen, then, as a mosaic of regions with different degrees of hydrophobicity, some more hydrophobic (PTFE coated) which can thus draw gas bubbles from the more hydrophilic ones (non-PTFE coated). Current density electrode potential curves obtained by the galvanostatic pulse method show three distinct regions. First, at low current densities (<10 mA/cm²), hydrogen is obtained at sufficiently low rates to diffuse away into the solution without bubble formation. In this region, PTFE coverage is not effective, and uncovered electrodes perform better than the coated ones. Above 10 mA/cm², the uncovered electrodes' overvoltage increases sharply due to bubble formation and concurrent loss of electroactive area. This is not observed in the

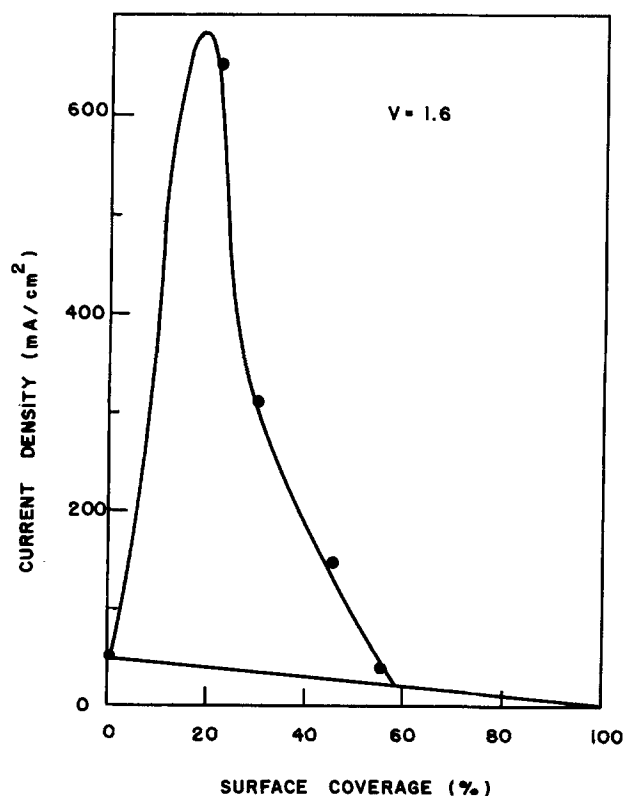


Fig. 3. Current densities versus surface coverage for a voltage of (A, left) $V = 1.2V \times Hg/HgO$ and (B, right) $V = 1.6V \times Hg/HgO$

coated electrodes, which perform better in this region because of the bubble scavenging action of the Teflon coated sites, as predicted by the Marangoni effect.

The size of the bubbles in the electrolyte increase when we have PTFE partial covered electrodes due to hydrophobicity of PTFE coating. The effect of the PTFE coverage on the cell ohmic resistance is discussed in Ref. (1).

Once formed in an electroactive (metallic) surface site, a gas bubble may stay there for a relatively long time until removed by convection, stirring, or flotation. A neighboring PTFE surface will cause bubble displacement, leading to lower total interfacial free energy and leaving metallic surface free for further action. Of course, this will not be observed when metal-electrolyte and PTFE-electrolyte contact angle are close.

At very high current densities ($>1 \text{ A/cm}^2$), violent bubble release and thermal convection should be the major factors leading to surface uncoverage. However, at the highest current density used in our experiments, most coated electrodes were more efficient than the uncoated ones.

Figures 3a and 3b showing current densities as a function of electrode surface coverage at given voltages (V) \times Hg/HgO can further elucidate the points under discussions. At $V = 1.2$, current densities decrease linearly with coverage, due to surface loss. The straight line between 0% and 100% coverage represents the expected behavior based on surface availability. At $V = 1.6$, current densities are up to 12 times larger than in uncovered electrodes, but they decrease at higher degrees of surface coverage.

Of course, at very high coverages, current densities should approach zero.

In this work, we chose to cover nickel electrodes with Teflon particles in the 10-100 μm size range, following a simple argument: gas bubbles in the 10 μm (and up) radius range should float rapidly in aqueous media. Bubbles much smaller than this would tend to remain dispersed in water, increasing electrolyte resistance and should thus be avoided. Further theoretical and experimental work is required to define the optimum Teflon-particle size and surface coverage to achieve lower electrode overvoltages.

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Technical Note



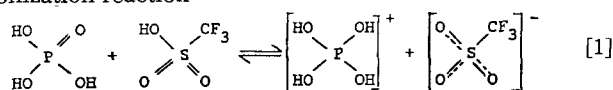
Ionization of Trifluoromethane Sulfonic Acid in Phosphoric Acid Raman Studies

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Much effort has been directed by various investigators (1-3) to optimize platinum catalysts for O_2 reduction in concentrated phosphoric acid. Relatively little attention, however, has been given so far to the acid-base properties of this electrolyte, and the possibility of modifying these properties so as to improve the current-voltage characteristics of platinum catalyzed O_2 cathodes. Through modifications of the acid-base properties, it may also be possible to increase the stability of dispersed Pt and slow down the oxidation of the carbon support.

The proton activity of concentrated H_3PO_4 can be controlled by treating the acid as a parent solvent system and changing its acid-base properties by the addition of strong acids and strong bases. Trifluoromethane sulfonic acid (TFMSA) is one of the strongest protonic acids (4) and, when added to concentrated H_3PO_4 , is expected to increase the proton activity according to the following ionization reaction



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In addition to providing a source of protons, this fluorinated acid may also increase the solubility and perhaps also the diffusion coefficient of O_2 . The solubility of O_2 in fluorinated solvents is known to be relatively high (5-8).

In the present work, the acid-base properties of the $\text{H}_3\text{PO}_4\text{-CF}_3\text{SO}_3\text{H}$ have been studied using Raman spectroscopy (for the first time).

Experimental

85% orthophosphoric acid was obtained from Mallinckrodt and purified by treating it first with hydrogen peroxide, then with hydrogen over Pt black, and finally by conventional pre-electrolysis. The details of this purification method have been described elsewhere (9). Higher concentrations of the acid were obtained by distilling water out of the 85% acid. TFMSA was purchased from Alfa-Ventron and distilled twice in an all-glass vessel in an N_2 environment before use. The first 10% of the distillate and last 10% of the residue were discarded. As obtained, the TFMSA was pale straw colored but the doubly distilled acid was colorless.

The Raman spectra were recorded with a Spex Ramanlog spectrometer and Coherent Radiation Model CR-8 argon ion laser. The power output of the laser was 150 mW at the sample at 514.5 nm. The $\text{C}13$ NMR spectra of the doubly distilled $\text{CF}_3\text{SO}_3\text{H}$ and also a 10% $\text{CF}_3\text{SO}_3\text{H}$ solu-