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June 1986

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INTERFACIAL PHENOMENA IN LOW
TEMPERATURE FUEL CELLS

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INTRODUCTION

A fuel cell is an electrochemical energy conversion device which converts chemical to electrical energy without the use of an intermediate mechanical (or Carnot) cycle. Since these devices are not Carnot limited, they can in principle operate at high conversion efficiency even at near-ambient temperature, e.g. a hydrogen-air cell has been operated at 70% thermal efficiency at 323 K for thousands of hours. In practice, there is a trade-off between efficiency and capital cost dictated by the intrinsic efficiency versus power density relation for any given configuration of materials of construction. Materials research influences the nature of this relation, which is the key to the economic competitiveness of this technology with respect to competing Carnot cycle devices. At the present time, it appears certain that low temperature (< 470⁰K) fuel cells will be the first type of fuel cell to penetrate the electric and/or gas utility market, probably to be superceded by high temperature (> 1000⁰K) technology some twenty years later. Japan has recently embarked on a particularly aggressive national effort to accelerate fuel cell development there in order to achieve a conversion of 16% of its base-load capacity to fuel cell power by the end of this century (!).

ELECTRODE MICROSTRUCTURE

Interfacial phenomena are central to all fuel cell technologies, but in this report I shall concentrate on those phenomena central to low temperature technologies. The critical action point in a fuel cell is in the gas-diffusion electrode, where gaseous and ionic reactants must

converge on a solid surface, react to form water and electrons, and electrons are carried away by the solid phase to the external circuit. A schematic diagram of these processes is shown in Fig. 1. Conceptually, it is clear that the solid catalyst surface is utilized more effectively if the solid surface is covered by a very thin film of electrolyte (the ionic reactant) than if it is fully immersed in bulk electrolyte. The interfacial chemistry of three-phase contact ("wetting") controls the microscopic structure of the electrode. The interfacial chemistry occurring in the processing of catalyst and polymer binder, the latter used to create gas pores and (ideally) control the contact angle of the electrolyte with the catalyst, is also critical in determining the microstructure created by the electrode fabrication.

ELECTROCATALYSIS

In addition to the interfacial chemistry that controls the transport processes of reactant to the catalyst surface, there is the equally important interfacial chemistry of the catalytic reaction, i.e. the electrocatalysis of the fuel and air electrode reactions. As in other chemical conversion technologies relying on catalysis, we are always looking for better (more efficient) and more cost effective catalysts for fuel cells. All fuel cell devices at present convert only hydrogen directly and not any form of hydrocarbon. This is not a fundamental limitation but a practical one due to the absence of a catalyst which provides direct conversion of hydrocarbons at a practical rate (and cell potential). Therefore, fuel cells have a fuel conditioning unit that converts a hydrocarbon fuel into a hydrogen rich gas that is fed to the

anode. This fuel conditioning unit adds to the capital cost and lowers the overall efficiency (the reforming reaction is endothermic). A catalyst providing direct oxidation of hydrocarbons at a cost effective rate (and cell potential) would significantly expand the commercial markets for fuel cells.

In spite of their higher unit cost, precious metals are the most cost effective catalysts for the air electrode. In their most cost effective form, the precious metal (Pt, Ir, Rh, Pd, or Au) is dispersed on a conducting support material (usually a graphite powder) to maximize the number of metal atoms at the surface. One expects the activity of the catalyst (in the absence of transport effects) to be linearly related to the specific noble metal surface area, since increasing the area per unit weight increases the fraction of metal atoms at the surface. What has been observed, however, is a non-linear dependence, shown in Fig. 2, with a maximum in activity at a surface area about one-third of the maximum possible metal area, and a net activity loss of about a factor of five from that projected from measurements on low area metal. Similar declines in catalytic activity of supported metals with increasing degree of dispersion have been observed in certain hydrocarbon reactions as well. Understanding and controlling this "size-dependent" reactivity in precious metal catalysis is vital to the intellectual growth of electrocatalysis as well as to the growth of fuel cells as a viable technology.

Significant progress has been made in recent years on the use of ultra-high resolution electron microscopy to determine surface structure

on "small" metal particles, small in this case being 10-50 nm. Based on the crystallite size-structure and size activity correlations from recent work, this author has postulated that there are three "regimes" of particle dimension representative of structure-activity relations in electrocatalysis:

- I. 10-50 nm and larger, macrocrystals terminated by facets of the low Miller index surface structure;
- II. 10-2 nm, microcrystals having "quasi-spherical" shapes formed from atomically stepped regions connecting isolated (111) facets;
- III. 2 nm and smaller, the metal cluster regime where unique electronic states may occur (one may also consider this quantum-mechanical regime).

It seems reasonable to conclude that variations in catalytic activity with crystallite size observed using Regime I and II type materials is related to the variation in intrinsic activity with atomic structure, i.e. so-called structure sensitivity. For electrocatalytic reactions, additional complications occur in the "metal cluster" Regime, particularly the stability of the metal towards dissolution. Such a destabilization can be expected even from classical thermodynamics, such

as the correction of the Nernst equation for a metal/metal-ion couple by the addition of a surface energy term (the Gibbs-Thompson relation). It may be that the projected near-zero activity for a monatomically dispersed catalyst is consistent with an expected spontaneous dissolution of the metal clusters in that state. From the foregoing discussion of supported metal studies, it seems clear that one should expect to see fairly sizeable variations in specific activity between the different low index surfaces of Pt, particularly between the (110)-2x1 and the (100) surface. However, single crystal experiments have been startling in the complexity of structure-property relations observed even for simple adsorption reactions, e.g. the adsorption of hydrogen. An example of this complexity is shown in Fig. 3, which is a voltammetry curve for Pt(111) in dilute sulphuric acid. According to conventional wisdom derived from polycrystalline electrodes, the voltammetric features occurring near the hydrogen electrode potential (0 - 0.3 V, RHE) correspond to hydrogen adsorption/desorption processes, those features at ca. 1V anodic correspond to adsorption/desorption of oxygenated species, and in the potential region in between corresponds to double-layer charging, i.e. no surface processes are occurring. On the highly ordered, clean (111) surface, however, a reversible surface process occurs in the so-called double-layer potential region, and no surface process occurs in the potential region where oxygen (hydroxyl) adsorption is expected. When the anodic potential limit is increased sufficiently to induce oxygen adsorption, one adsorption occurs all the apparently anomalous features disappear (!) concomitant with the growth of

"expected" features. Neither the chemistry of these new processes nor the cause of their disappearance is as yet understood. UHV surface analytical methods (9) were used to produce the highly ordered (111) surfaces, and LEED analysis has been used to determine perturbations to the surface structure caused by oxygen (hydroxyl) adsorption. It appears that the new processes are associated with atomically flat regions of the (111) surface with a critical region size that is quite large, at least 10 nm or more. The chemistry in this process is not known, and from the possible known chemistries, none would seem to require a large critical ensemble. Electrochemistry is now faced with a perplexing set of observations that appear to require very new concepts of interfacial chemistry at metal electrode surfaces.

At the present state of study of Pt single crystals, with their anomalous behavior there seems to be no connection between the electrochemistry at these "ideal" surfaces and the "real" surfaces which form on the supported metals. Not enough is known about the surface structure on supported metal crystallites to know whether the lack of connection is fundamental or not, i.e. is not due to experimental factors associated with the special procedures used with single crystals. It is this author's opinion that progress in this area of science is going to be very slow. Answers to the right questions will require the use of very expensive instrumentation (dedicated UHV analytical systems, modified states on high resolution electron microscopes, dedicated scanning tunneling microscopes) and collaboration with specialists in techniques/instrumentation, both of these requirements being problematic

in times of budget reductions.

METAL DISSOLUTION AND RELATED PHENOMENA

Another interfacial phenomenon vital to the commercial viability of fuel cells is the maintenance of noble metal area over the lifetime of the device. The loss of metal dispersion, more frequently referred to as "sintering", in an ionic medium can be distinguished from thermal sintering in vacuum or in a gaseous environment. There are two general mechanisms usually considered in the analysis of sintering: the coalescence of metal particles colliding during migration on the support, and the transport of atoms from small particles to large particles similar to the Ostwald ripening of colloidal solutions. The first process is analogous to a two-dimension Brownian motion of metal particles on the support surface, with random collisions and subsequent coalescence. The Ostwald ripening model for thermal sintering is usually interpreted as occurring via ad-atoms or ad-molecules hopping from small particles onto the support surface, migrating across the support to larger particles and there incorporated. The transfer of atoms from a particle onto the support is a highly activated process, and might be expected to occur only at relatively high temperature. The corresponding Ostwald ripening mechanism for an electrocatalyst is depicted in Fig. 4. In an electrocatalyst, the Ostwald ripening mechanism can occur via ionic species either directly through solution or by surface diffusion. The ionic species would be the solvated metal ion, and the net process is really dissolution-deposition driven by the effect of curvature of the metal surface on the metal/ion potential, the correction of the Nernst

equation by a Gibbs-Thompson relation. The electrical potential gradient at the surface in effect replaces the thermal energy required to remove metal atoms from the surface, so that one might expect Ostwald ripening to occur for electrocatalysts even at low ($< 200^{\circ}\text{C}$) temperatures. The dissolution-deposition process should clearly be potential dependent, which should make it a relatively easy mechanism to identify.

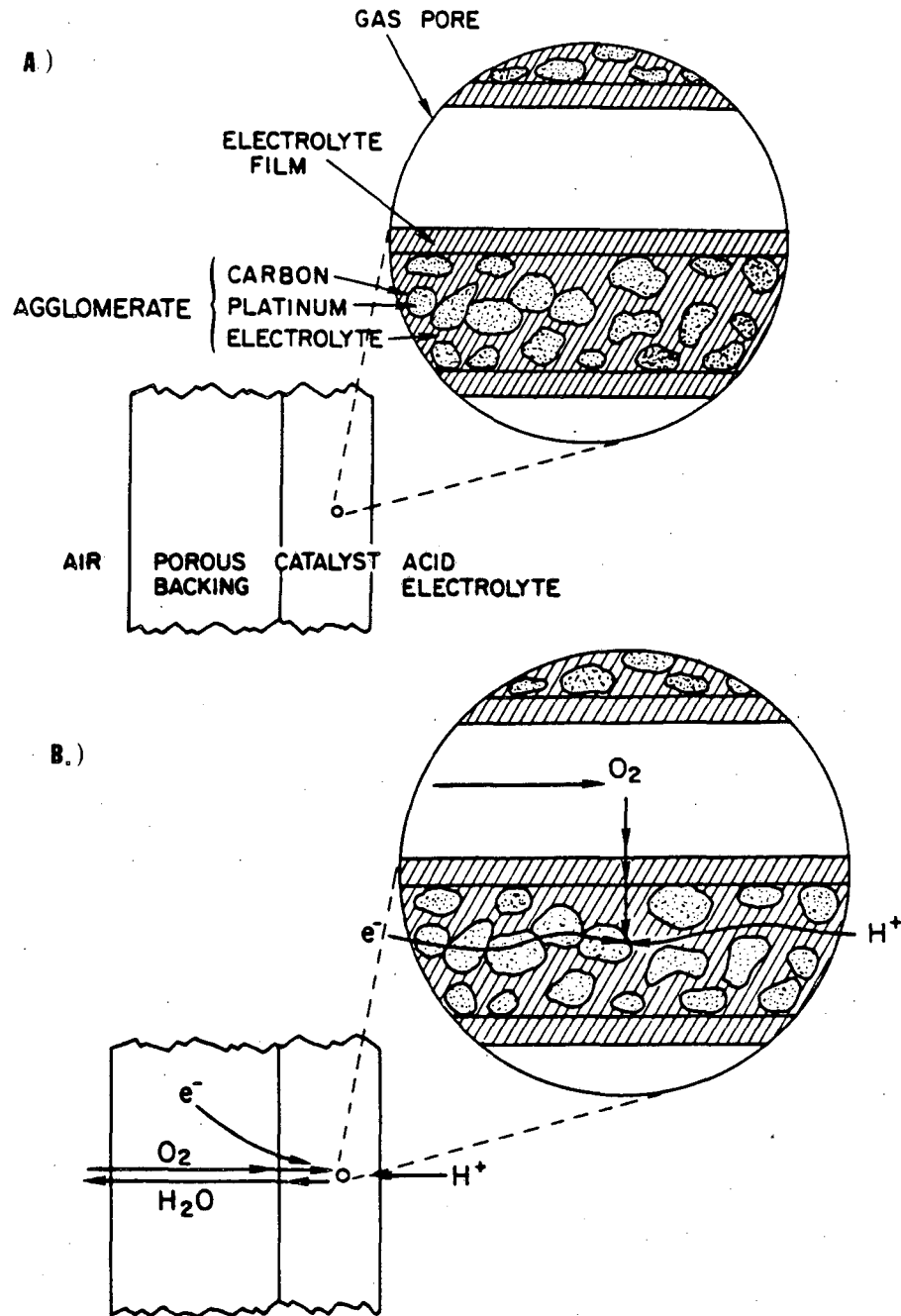
Some studies have been made using platinum fuel cell type catalysts comparing sintering of the platinum in both gas-phase and liquid-phase environments. At the same temperature, the rate in all the liquid media were at least an order of magnitude higher than in vacuum or inert atmosphere. Surprisingly, the rate did not change dramatically between polar and non-polar solvents, nor was the rate appreciably different in electrolytes than non-electrolytes. Consistent with these observations is the report by some investigators that the sintering in phosphoric acid at typical fuel cell conditions is not potential dependent (!). Some investigators have concluded that an Ostwald ripening process occurs, but via adatoms and not solvated ions, i.e. an exact equivalent of the thermal sintering of supported metals in the gas-phase. They have suggested that liquids act as a bridge for the transfer of Pt atoms from particles to the support, but were unable to provide a more detailed picture of the nature of this "bridge". Much more experimental work is clearly called for to explain these apparently conflicting and unexpected observations in this area of interfacial chemistry.

Closely related to the interfacial chemistry of Ostwald ripening is the generic area of the solution thermodynamics of small metal

crystallites. Solubility data for the precious metals in strong electrolytes is seriously lacking, as are effects on solubility of anion (or cation), concentration, and crystallite size. There may also be effects on solubility of impurities in the electrolyte, e.g. impurity anions like Cl^- that have a complexing effect, or large impurity cations that may have a salting-out effect. An effect of crystallite size on solubility is expected from classical thermodynamics, the Kelvin equation, but this expectation has never been confirmed experimentally for metals. Careful experimental studies on precious metal solubility are clearly needed, and the personnel and apparatus needed for such studies are not now present at fuel cell development facilities.

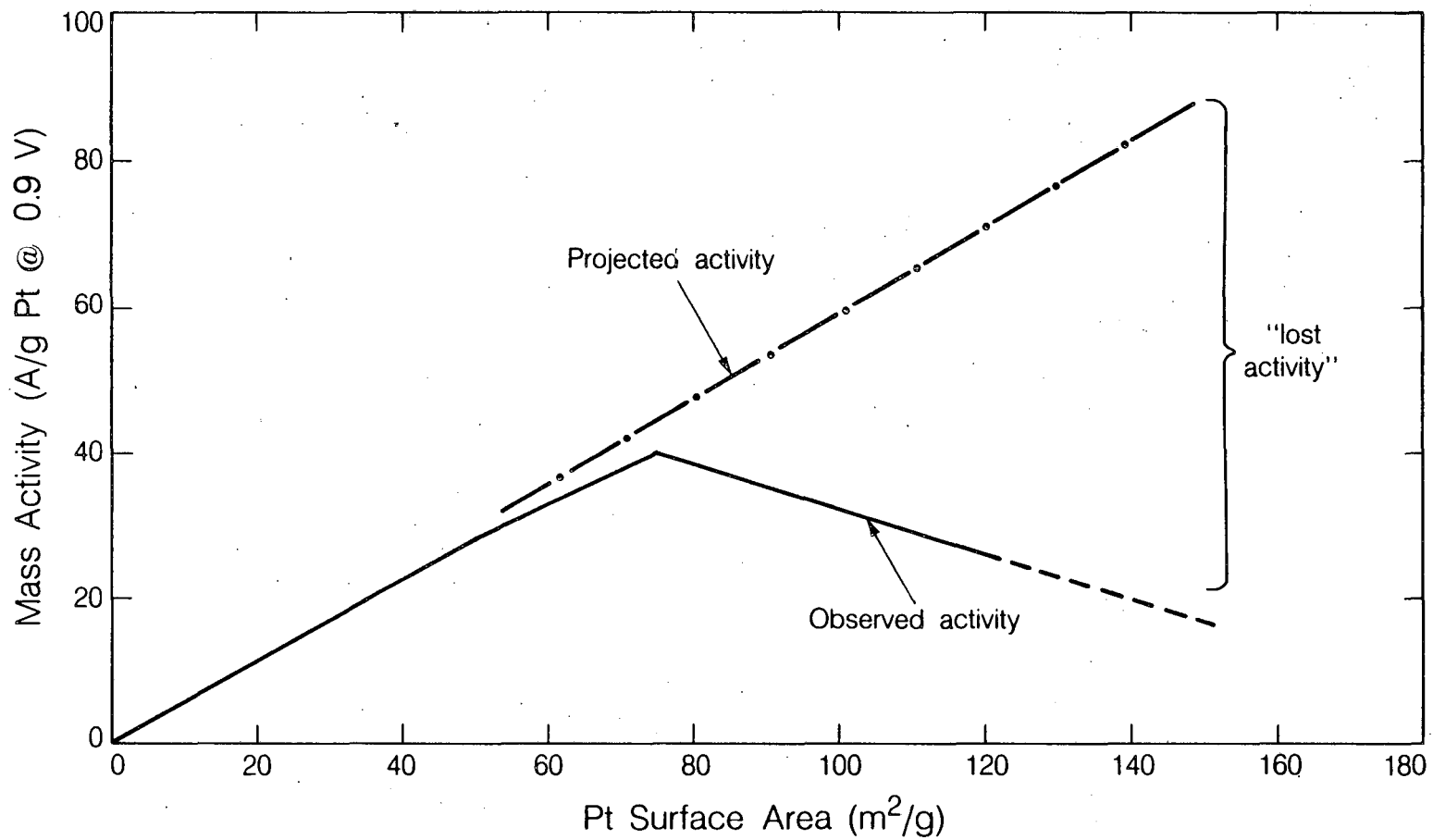
RESEARCH RECOMMENDATIONS

<u>Interfacial phenomena</u>	<u>Related generic research areas</u>	<u>Relevant academic disciplines</u>
Electrode microstructure	o Contact angle measurements in composite materials	materials science and chemical engineering
	o Novel thin-film fabricated structures	materials science
	o Polymer-graphite composite structure studies	materials science
Electrocatalysis	o Novel catalysts for direct hydrocarbon oxidation	organometallic chemistry and physical chemistry
	o Structure determination of small metal clusters	materials science
	o Single crystal electrochemistry	physical chemistry
Metal Dissolution	o Definitive parametric solubility determinations	materials science



XBL 866-2410

Figure 1. Schematic representations of a gas-diffusion electrode structure (a.) and the transport processes (b.) occurring within the structure.



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Figure 2. Activity - Pt surface area correlation observed with phosphoric acid fuel cell cathodes.

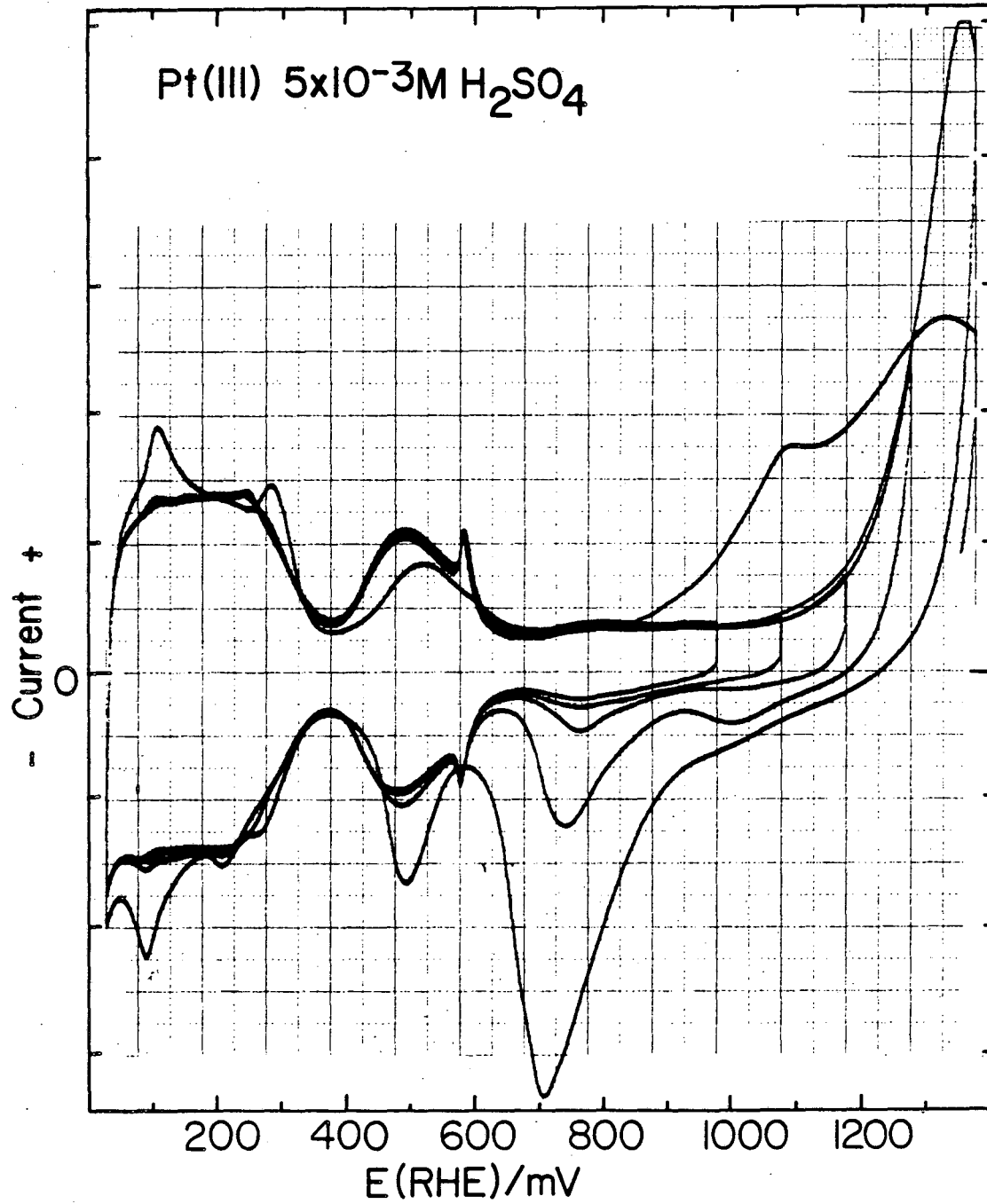
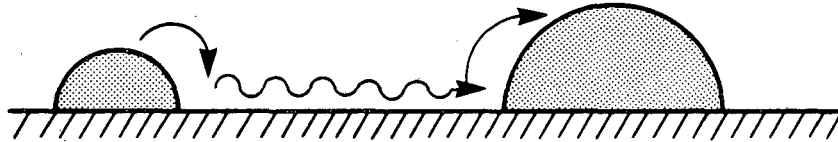


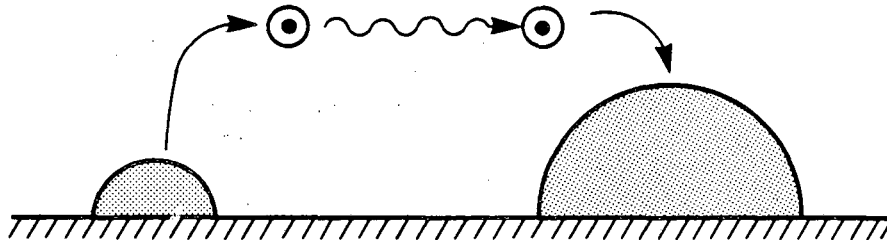
Figure 3. Voltammetry of UHV prepared Pt(111) surface.

Ostwald Ripening

Conventional Catalyst:



Electrocatalyst:



⊙ ≡ solvated metal ion

XBL 859-10745

Figure 4. Conceptual representations of Ostwald ripening processes with supported metal catalysts.

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