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01 May 1999

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Charles C. Chusuei

Missouri University of Science and Technology, [chusuei@mst.edu](mailto:chusuei@mst.edu)

T. S. Murrell

J. S. Corneille

M. G. Nooney

*et. al.* For a complete list of authors, see [https://scholarsmine.mst.edu/chem\\_facwork/699](https://scholarsmine.mst.edu/chem_facwork/699)

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### Recommended Citation

C. C. Chusuei et al., "Liquid Reaction Apparatus for Surface Analysis," *Review of Scientific Instruments*, vol. 70, no. 5, pp. 2462-2464, American Institute of Physics (AIP), May 1999.

The definitive version is available at <https://doi.org/10.1063/1.1149778>

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## Liquid reaction apparatus for surface analysis

C. C. Chusuei, T. S. Murrell,<sup>a)</sup> J. S. Corneille, M. G. Nooney, S. M. Vesecky,  
L. R. Hossner,<sup>a)</sup> and D. W. Goodman<sup>b)</sup>

*Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012*

(Received 1 December 1998; accepted for publication 25 January 1999)

A design for a liquid reaction apparatus is described which allows surfaces prepared in ultrahigh vacuum (UHV) to be reacted with solutions of a wide *pH* range under dry nitrogen atmosphere and subsequently returned to UHV for surface analysis. © 1999 American Institute of Physics. [S0034-6748(99)02305-9]

### I. INTRODUCTION

Research in our surface science laboratory has recently expanded to include interdisciplinary studies pertaining to solid-liquid reaction studies relevant to biomineralization<sup>1</sup> and soil chemistry<sup>2</sup> on metal oxide surfaces. Soil chemists have investigated adsorption phenomena by reacting solutions with powder samples of naturally occurring or synthetic soil components.<sup>3,4</sup> Similarly, in the study of biomineralization, Brunauer-Emmett-Teller (BET) characterized colloidal seeds have been used to model the metal-oxide surfaces of artificial implants.<sup>5</sup> Because of the porosity of the supports, probing these model oxides is not amenable to surface analytical techniques. Ideally, metal oxide surfaces pertaining to these studies would be prepared in ultrahigh vacuum (UHV) on flat surfaces. Synthesis of thin film oxides are desirable since they overcome surface charging problems, and are ideal for modeling natural metal oxide particulates in soils<sup>6</sup> and metal oxide surfaces used in implants.<sup>5</sup> The challenge, for both areas of study, is to develop a system in which these thin film samples could be reacted with solutions via solid-liquid adsorption of widely varying compositions with minimal contamination from exposure to air.

In the last few decades electrochemical cells have been interfaced with UHV chambers for examining electrode surfaces using surface sensitive methods.<sup>7-11</sup> These setups have bridged the gap between electrochemical and surface sensitive analysis. Likewise, an apparatus that permits the solid surface to be exposed to liquid (at laminar flow conditions insuring fresh solid-liquid surface exposures) in inert atmosphere and then transferring into UHV for surface analysis should prove to be useful for studies relevant to biomineralization and soil chemistry. Here we describe a system for conducting solid-solution reactions under well-controlled conditions at atmospheric pressure that can be interfaced with an UHV system. In this simple design, surfaces are grown and characterized in UHV and then transferred to a liquid reaction cell for exposure to solutions. The liquid reaction system

may be divided into three major components: (1) the UHV surface analysis chamber, (2) the liquid reaction cell, and (3) the antechamber.

### II. APPARATUS

The liquid reaction cell (Fig. 1), mounted onto the electrochemical UHV chamber fully described elsewhere,<sup>10</sup> provides a controlled environment for solid-liquid reactions. Figure 1 shows a side view of the liquid cell. Figure 2 shows a plan view of its operation in relation to the peristaltic pump and solution container. The cell is purged with N<sub>2</sub> during reactions to prevent atmospheric contamination. The sample is brought into contact with a meniscus of flowing solution during adsorption experiments. This continuous flow of solution provides fresh, unreacted solution to the surface during experiments. Excess, reacted solution spills over to a drain and exits the system. Upon completion of a liquid reaction, the meniscus is removed from the sample surface and any residual solution remaining on the surface is blown off with dry N<sub>2</sub>.

The sample is mounted on an Insulator Seal Inc. thermocouple (TC)-power feedthrough (part No. 9391012) welded to a 1-in. outer diam. (o.d.) stainless steel tube. The single-crystal sample mount is comprised of support legs and heater wires. Two [0.010-in.-diam] Ta wires were bent in the shape of a U and spot welded to the 0.060-in. diam Ta wires, which are attached to the copper power leads of the ceramic feedthrough and function as the support legs. The sample is spot welded to the 0.010-in.-diam Ta wire. Sample temperatures, which can be increased to as high as 1500 K for temperature programmed desorption experiments by passing current through the leads, are monitored with a W-5%Re/W-26%Re TC spot welded to the back of the sample. The TC is bent upward at the spot weld to keep the wires from touching the solution, allowing only the face of the sample to contact the solution. The primary component of the liquid reaction cell is a Teflon column. Teflon was selected because solutions in liquid reaction experiments incorporate a wide *pH* range. If glass had been used, silicates could dissolve in solutions with a basic *pH*. The combination of the N<sub>2</sub> jet (Fig. 1) along with sparging of the solution via fritted glass with dry N<sub>2</sub> maintains a slightly positive pressure that offsets

<sup>a)</sup>Also with: Department of Soil & Crop Sciences, Texas A&M University, College Station, TX 77843-2474.

<sup>b)</sup>Author to whom correspondence should be addressed; electronic mail: GOODMAN@MAIL.CHEM.TAMU.EDU

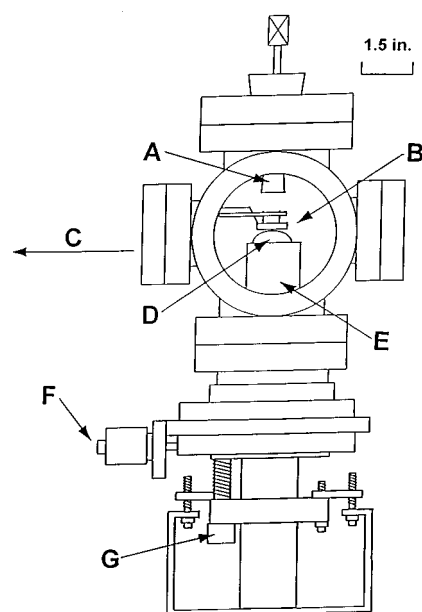


FIG. 1. Schematic of the liquid reaction cell: (A)  $N_2$  jet providing inert atmosphere, (B) sample, (C) path to antechamber, (D) meniscus of flowing solution, (E) Teflon column which is more fully depicted in Fig. 3, (F) X, Y direction micrometer, and (G) Z direction micrometer.

$O_2$  diffusion through the Teflon from the atmosphere. The column is constructed from a Teflon cylinder 12-in.-long with 1.62-in.-diam. A 0.50-in.-diam hole drilled 11 in. deep in the center with a volume of  $\sim 35$  mL serves as the solution delivery tube. Overflow (Fig. 2) is routed to a drain hole via a collection channel 0.75-in.-deep surrounding the delivery tube. The channel has a 0.75-in. inner diam (i.d.) and a 1.38-in. o.d. The dimensions of this channel leave a 0.12-in.-thick lip around the delivery tube, which aids in the production of a meniscus as the solution overflows. At the bottom of the overflow channel is a drain hole with a 0.25-in.-diam. An OMEGAFLEX<sup>TM</sup> peristaltic pump provides regulated solution flow (115 VAC, 60 Hz induction motor) with a solution delivery rate of  $5 \text{ mL min}^{-1}$ , giving a continuous fresh liquid

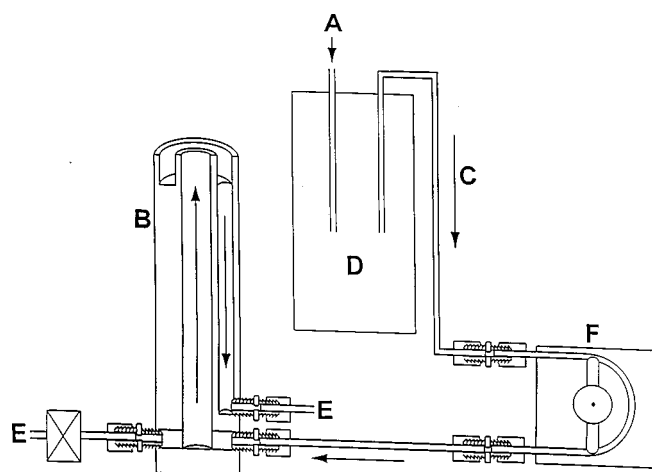


FIG. 2. Stylized drawing of components used for the delivery of solution to the Teflon solution cell (not to scale). The cell itself is depicted with the top rotated slightly toward the viewer to clarify the location of the solution delivery tube and drain channel: (A)  $N_2$  in flow, (B) Teflon cell, (C) direction of solution flow, (D) solution, (E) to drain, and (F) peristaltic pump.

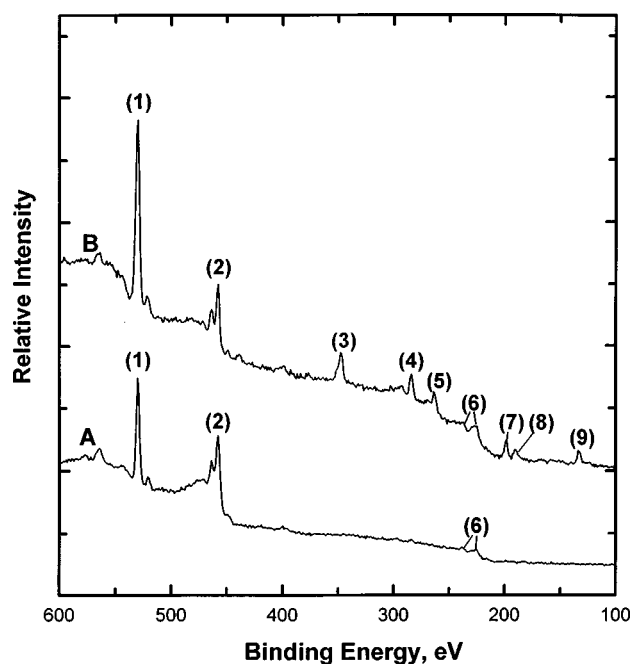


FIG. 3. XPS survey scans of: (A) a freshly prepared titania ( $TiO_2$ ) thin film on a polycrystalline Ta support and (B) the thin film after exposure to a phosphate solution for 3 h prior to reintroduction into the UHV. The peak assignments of the core levels are as follows: (1)  $\sim 530$  eV, O  $1s$ , (2)  $\sim 458$  eV, Ti  $2p$ , (3)  $\sim 348$  eV, Ca  $2p$ , (5)  $\sim 284$  eV, Cl  $1s$ , (6)  $\sim 245$  eV, Ta  $4d$ , (7)  $\sim 200$  eV, Cl  $2p$ , (8)  $\sim 191$  eV, P  $2s$  and (9)  $\sim 134$  eV, P  $2p$ .

surface to be exposed to the substrate prior to surface analysis. Solutions used in experiments are stored in a 1 L Nalgene wide mouth bottle which accommodates ion selective electrodes for pH solution adjustment. Teflon tubing (0.25-in. o.d.) is inserted into two 0.25-in.-diam holes in the screw cap of the Nalgene bottle. One Teflon tube, connected to a  $N_2$  line, sparges the solution. The other tube delivers solution to the peristaltic pump and transfers solution from the pump to the cell.

The sample may be moved from atmospheric to UHV conditions while maintaining UHV in the analysis chamber and atmospheric pressure in the liquid cell. This is achieved by moving the sample translator through a pair of differentially pumped, spring-loaded Teflon seals in the antechamber.<sup>12</sup> A MDC C-LOC gate valve on a 2.75 in. conflat flange seals the antechamber on the atmospheric side and can be opened for sample translation. After a liquid reaction experiment, the sample can be returned to the antechamber and rough pumped by an Alcatel 2004A mechanical forepump with a pumping speed of  $5.4 \text{ m}^3 \text{ h}^{-1}$ . Once the pressure reaches the  $10^{-3}$  Torr range, a Balzers 50 L/s turbopump can then be valved in via a right angle elastomer valve connecting the turbopump to the antechamber. The turbopump allows the antechamber to be brought into the low  $10^{-7}$  Torr range (in approximately 2 h from the  $10^{-3}$  Torr range) prior to transferring the sample into the UHV chamber for surface analysis. In solid-liquid adsorption experiments where species are weakly bound to the surface, appreciable amounts of material may be removed by the pumping action. Hence, this apparatus would not be amenable for

studying systems in which physisorption or physisorbed reactants play a dominant role on the surface.

### III. MEASUREMENTS

Clean conditions attainable with this apparatus are shown in the following x-ray photoelectron spectroscopy (XPS) survey scans. Figure 3(A) shows a clean thin-film TiO<sub>2</sub> vapor deposited (~50 Å thick) onto a Ta substrate; only O and Ti are present as denoted by peaks (1) and (2), respectively. The freshly prepared film was then translated to the solution cell and exposed to a phosphate solution at pH 6.5, ionic strength  $\mu=0.01$  M using NaCl as background electrolyte and 119  $\mu\text{g mL}^{-1}$  P as KH<sub>2</sub>PO<sub>4</sub> for 3 h. Subsequent XPS analysis [Fig. 3(B)] shows minimal carbon contamination at the surface after a 3 h exposure to solution (less than 20 at %). The deposition of calcium phosphate on titania via solid-liquid adsorption using the apparatus is clearly seen in peaks (3), (8), and (9).

### ACKNOWLEDGMENTS

Support for this work was provided by Laboratory Directed Research and Development funding from the Pacific

Northwest National Laboratory (PNNL), operated by Battelle. C.C.C. gratefully acknowledges support from the Associated Western Universities, Inc. and PNNL

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