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Quartz Crystal Microbalance Studies of Electrochemical Growth
of Conducting Polymers

by

Katsuhiko Naoi, Mary M. Lien and William H. Smyrl.

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Corrosion Research Center
Department of Chemical Engineering and Materials Science
221 Church St. SE
University of Minnesota
Minneapolis, MN 55455

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p style="margin-top: 10px;"> In-situ monitoring of the mass change occurring during electrochemical growth of conducting polymers is possible by use of QCM. The mass change due to polymer formation as well as doping of anions and solvent up-take are monitored with time. Electro-polymerization factors, such as electrolysis mode (galvanostatic, potentiostatic, scan, pulse), electrolyte, solvent are compared and the electrochemistry of the resulting film has been examined. QCM/Potentiostatic measurements have the advantage of providing simultaneous mass change and charge data. From these, 2 distinct growth phases are observed a fast, charge-efficient growth on substrate and a slower, inefficient growth on pyrrole. </p>											
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Quartz Crystal Microbalance Studies of Electrochemical Growth of Conducting Polymers

Katsuhiko Naoi, Mary Lien and William H. Smyrl

Corrosion Research Center,
Department of Chem. Eng. & Mat. Sci., University of Minnesota,
221 Church St. SE, Minnesota 55455 U.S.A.

Utilization of the quartz crystal microbalance (QCM) in conjunction with electrochemistry can allow one to determine the mass of polymer electrode and charge utilization simultaneously or in-situ under the conditions that the electrode is polarized electrochemically. This combination of measurements has already been used for the following cases; 1. electrode deposition of metals (1); 2. dissolution of metals (Ni)(2); 3. Redox process for conducting polymer (polypyrrole)(3), polyaniline(4) and redox polymers (polyvinylferrocene)(5). The method is also advantageous for the monitoring of the mass change of conducting polymers like polypyrrole, polyaniline, etc. either during the redox process or during electropolymerization. The emphasis of this paper is to monitor polymer growth on the electrode with time, and to investigate the growth rate of polypyrrole and the coulombic efficiency of electropolymerization as a function of time.

Shear mode 6MHz AT-cut quartz crystals were used for this investigation. They were obtained from Inficon (East Syracuse, NY). The crystals had vacuum deposited gold electrodes on both sides. The total projected area exposed to the solution was 0.33 cm². The crystal oscillator circuit included a power source and an oscillator (Inficon XTC). The frequency was measured with a frequency counter (HP5344A). The frequency measurements were sent to and stored in a personal computer (HP9816). The experiments were carried out in a 4-necked glass cell. Two of the necks were used for the gas inlet and outlet, one for the reference electrode and the last one for the counter electrode (stainless steel/large surface area). The working electrode was the conducting polymer film in contact with the solution. The quartz plate was sealed to the cell with a silicone rubber sealant. The electrode potential was controlled by a potentiostat. The working electrode was grounded through the potentiostat. The oscillator was isolated from the potentiostat with a 1 μ F capacitor (Figure 1).

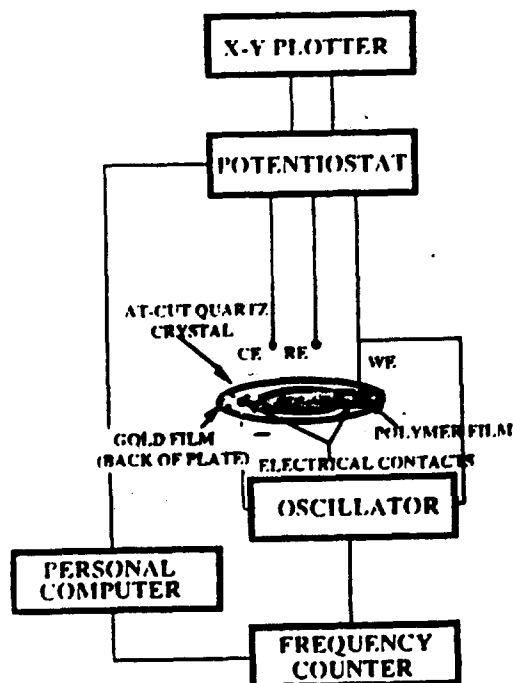


Fig. 1 Quartz crystal microbalance experimental apparatus(6)

QCM/Electrochemical measurements on the growth rate of conducting polymers were performed under the following conditions:

- 1) Galvanostatic
- 2) Potentiostatic
- 3) Potential Sweep
- 4) Potential Pulse

For example, under potentiostatic conditions, polypyrrole growth and total charge consumed have been monitored as a function of time. Two distinct growth regions corresponding to the polymer growth on bare substrate (fast, charge efficient) and polymer growth on polymer (slow, charge inefficient) have been observed (Figure 2).

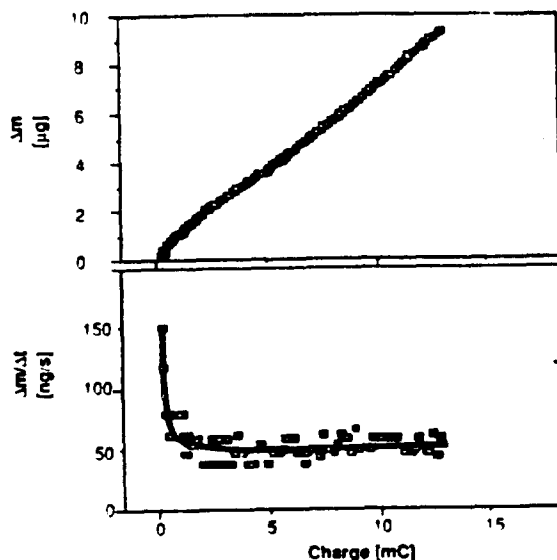


Fig. 2 Dependence of mass change (Δm) and growth rate ($\Delta m/\Delta t$) with passed charge consumed for the polypyrrole electropolymerization

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