ELECTROCHEMISTRY OF FERROELECTRIC THIN FILM $PbZr_{0.52}Ti_{0.48}O_3$ IN H_2SO_4

By

Leo J. Small

A Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: MATERIALS SCIENCE AND ENGINEERING

Approved by the
Examining Committee:

Dr. David J. Duquette, Thesis Adviser

Dr. Douglas Chrisey, Member

Dr. Daniel Gall, Member

Dr. Joel Plawsky, Member

Dr. Christopher Apblett, Member

Dr. Jon Ihlefeld, Member

Rensselaer Polytechnic Institute
Troy, New York

November 2012
(For Graduation December 2012)

ABSTRACT

Remote sensing applications in harsh environments require sensor materials appropriately matched to the environment. $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) is a candidate for remote sensing applications, where it could be used as both a sensor and power source. In this light, the evolution of the PZT-H_2SO_4 interface is explored at low pHs. A robotic microdroplet cell is developed to differentiate the electrochemical response of the cracks and pores inherent to the PZT film from that of continuous PZT. Accelerated chemical attack is observed at the pores, while the continuous PZT displays electrochemical hysteresis; the ferroelectric-solution interface can be switched between two different charge states at a given potential. As time progresses, electrochemical impedance spectroscopy reveals a change in the structure of the PZT-H_2SO_4 interface. Development of equivalent circuits to model the competing processes of pore growth, interfacial layer formation, and uniform chemical attack are guided by the evolution of film structure and chemistry as observed *ex-situ* with scanning electron microscopy, x-ray photoelectron spectroscopy, and x-ray diffraction. The Point Defect Model for the passive state is used to explain the dissolution processes observed in the complex oxide. Application of this model to $PbZr_xTi_{1-x}O_3$ for x = 0.25, 0.52, and 0.95 points to the role of titanium in the creation of an ionically insulating layer that impedes further chemical attack.