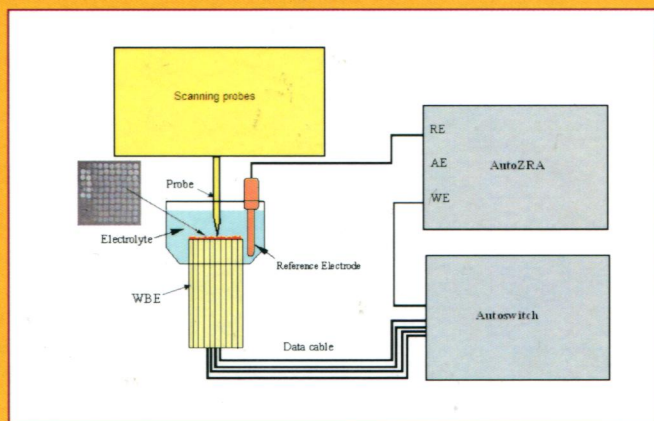


Wiley Series in Corrosion
R. Winston Revie, Series Editor

HETEROGENEOUS ELECTRODE PROCESSES AND LOCALIZED CORROSION



YONGJUN TAN

Copyright © 2013 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Tan, Yongjun, 1963–

Heterogeneous electrode processes and localized corrosion / Yongjun Tan.

pages cm. – (Wiley series in corrosion)

Includes bibliographical references and index.

ISBN 978-0-470-64795-0 (hardback)

1. Corrosion and anti-corrosives. 2. Heterogeneous catalysis. 3.

Electrocatalysis. I. Title.

TA418.74.T36 2013

620.1'1223–dc23

2012020902

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Contents

Preface	ix
1. Homogeneous Electrode Models and Uniform Corrosion Measurements	1
1.1 Homogeneous Electrodes and Traditional Electrochemical Methods / 3	
1.2 Mixed Electrodes and Uniform Corrosion Models / 7	
1.3 Mixed Potential Theory and Electrochemical Corrosion Measurement / 10	
1.4 Electrochemical Impedance Investigation of an Electrode–Solution Interface / 19	
1.5 Electrochemical Noise Monitoring of Rapid Electrode Processes / 26	
1.6 Issues and Difficulties in Traditional Electrochemical Methods / 31	
References / 32	
2. Probing Electrode Inhomogeneity, Electrochemical Heterogeneity, and Localized Corrosion	37
2.1 Probing Electrode Inhomogeneity / 39	
2.2 Probing Electrochemical Heterogeneity and Localized Corrosion / 44	

2.3 Overview of Various Techniques for Probing Localized Corrosion / 48

References / 61

3. Visualizing Localized Corrosion Using Electrochemically Integrated Multielectrode Arrays 67

3.1 An Electrochemically Integrated Multielectrode Array: The Wire Beam Electrode / 70

3.2 Visualizing the Progression of Localized Corrosion in an Evans Water Drop / 76

3.3 Visualizing Localized Corrosion in Nonuniform Environments with Ion Concentration Gradients / 84

3.4 Visualizing Localized Corrosion by a WBE in Conjunction with Scanning Probes / 91

References / 99

4. Measuring Thermodynamic and Kinetic Parameters from Localized Corrosion Processes 101

4.1 Methods of Probing Localized Corrosion Thermodynamics and Kinetics / 103

4.2 Measuring Localized Corrosion Using the Overpotential–Galvanic Current Method / 109

4.3 Measuring Localized Corrosion Using the Galvanic Current Method / 120

4.4 Measuring Localized Corrosion Using the R_{ii} –WBE Method / 125

References / 131

5. Characterizing Inhomogeneity and Localized Corrosion on Coated Electrode Surfaces 135

5.1 Characterizing Inhomogeneities in Organic Coatings and Inhibitor Films / 137

5.2 Characterizing Inhomogeneity in Organic Coatings Using the WBE Method / 141

5.3 The Effects of Coating Inhomogeneity on Electrochemical Measurement / 145

5.4 Visualizing Underfilm Corrosion and the Effects of Cathodic Protection / 148

5.5 Studying Corrosion Protection by Coatings and Cathodic Protection / 155

References / 157

6. Designing Experiments for Studying Localized Corrosion and Its Inhibition in Inhomogeneous Media **161**

- 6.1 Basic Issues in Localized Corrosion and Inhibitor Test Design / 162
- 6.2 Fundamental Considerations in Selecting Corrosion Measurement Techniques / 165
- 6.3 Designing Corrosion Tests in Highly Resistive and Inhomogeneous Media / 168
- 6.4 Case Studies: Designing Crevice Corrosion Tests by Means of a WBE / 181
- 6.5 Case Study: Designing Experiments for Localized Corrosion Inhibitor Discovery / 186

References / 190

7. Sensing Localized Electrodeposition and Electrodeposition **195**

- 7.1 Experimental Methods for Sensing Localized Electrodeposition and Dissolution / 197
- 7.2 Sensing Localized Electrodeposition Using a WBE / 200
- 7.3 Sensing Localized Electrodeposition Using a WBE / 204
- 7.4 Sensing Nonuniform Electrochemical Deposition of Organic Coatings / 211

References / 216

8. Versatile Heterogeneous Electrode Processes **219**

- 8.1 Scanning and Modeling Various Heterogeneous Electrode Processes / 222
- 8.2 Electrochemical Noise Generation from Electrochemical Heterogeneity / 225
- 8.3 Harvesting Electrical Power from Electrochemical Heterogeneity Using a WBE / 231
- 8.4 Further Research Issues in Electrochemical Heterogeneity / 237

References / 238

Index

243