Contents

Series Preface xi Preface xiii

- 1Introductory Perspectives1A. Paul Alivisatos and Wojciech T. OsowieckiReferences4
- 2 The Joint Center for Energy Storage Research: A New Paradigm of Research, Development, and Demonstration 7

Thomas J. Carney, Devin S. Hodge, Lynn Trahey, and Fikile R. Brushett

v

- 2.1 Background and Motivation 7
- 2.2 Lithium-ion Batteries: Current State of the Art 8
- 2.3 Beyond Li-Ion Batteries 9
- 2.4 JCESR Legacies and a New Paradigm for Research 9
- 2.5 The JCESR Team 13
- 2.6 JCESR Operational Tools 16
- 2.7 Intellectual Property Management 17
- 2.8 Communication Tools 17
- 2.9 JCESR Change Decision Process 17
- 2.10 Safety in JCESR 19
- 2.11 Battery Technology Readiness Level 20
- 2.12 JCESR Deliverables 21
- 2.13 Scientific Tools in JCESR 22
- 2.14 Techno-economic Modeling 23
- 2.14.1 Techno-economic Modeling of a Metal–Air System for Transportation Applications 23
- 2.14.2 Techno-economic Modeling of Flow Batteries for Grid Storage Applications 25
- 2.15 The Electrochemical Discovery Laboratory 27
- 2.15.1 The Effect of Trace Water on Beyond Li-ion Devices 27
- 2.15.2 Stability of Redox Active Molecules 28
- 2.16 Electrolyte Genome 28
- 2.16.1 Screening of Redox Active Molecules for Redox Flow 29
- 2.16.2 Examination of Multivalent Intercalation Materials 30

vi Contents

2.17	Combining the Electrolyte Genome with Techno-economic
	Modeling 31
2.18	Prototype Development 31
2.19	Legacy of JCESR 33
2.20	Conclusion 34
	Acknowledgments 34
	References 34
3	Determination of Redox Reaction Mechanisms in
	Lithium–Sulfur Batteries 41
	Kevin H. Wujcik, Dunyang R. Wang, Alexander A. Teran, Eduard Nasybulin,
	Tod A. Pascal, David Prendergast, and Nitash P. Balsara
3.1	Basics of Lithium–Sulfur Chemistry 41
3.2	End Products of Electrochemical Reactions in
	the Sulfur Cathode 44
3.3	Intermediate Products of Electrochemical Reactions in
	the Sulfur Cathode 45
3.3.1	Reactions of $S_{0} = 45$
3.3.2	Reactions of Li ₈ 46
3.3.3	Reactions of Li ₂ S ₄ 47
3.3.4	Reactions of Li_2S_4 48
335	Production of Radical Anions 49
3.4	Fingerprinting Lithium Polysulfide Intermediates 49
341	X-ray Absorption Spectroscopy 50
342	Flectron Paramagnetic Resonance Spectroscopy 53
343	LIV-Vis Spectroscopy 54
344	Baman Spectroscopy 57
3.1.1 3.4.5	Nuclear Magnetic Resonance Spectroscopy 57
25	In Situ Spectroscopic Studies of Li S Betterios 59
3.5 3.5.1	Y ray Absorption Spectroscopy 58
3.5.1	Flactron Daramagnetic Resonance Spectroscopy 50
252	LIV Vis Spectroscopy 60
5.5.5 2 E 4	Demon Spectroscopy 60
3.3.4 2 F F	Nuclear Magnetic Decompose Spectroscopy 60
3.3.3 2.C	Nuclear Magnetic Resonance Spectroscopy 61
3.6	C l l considerations 62
3./	Concluding Remarks 64
	Acknowledgment 68
	References 68
4	From the Lab to Caling up This Film Color Absorbers 75
4	From the Lab to Scaling-up Thin Finit Solar Absorbers 75
	Harikila Deligianni, Ludomyr I. Romankiw, Daniel Lincol, and Diama Dhilinga Cuan d
4.1	
4.1	Introduction /5
4.2	State-of-the-art Electrodeposition for Photovoltaics 79
4.2.1	Electrodeposited CulnGaSe ₂ (CIGS) 80
4.2.1.1	Metal Layers 80
4.2.1.2	Electrodeposition of Copper 81

- 4.2.1.3 Electrodeposition of Indium 82
- 4.2.1.4 Electrodeposition of Gallium 85
- 4.2.2 Single Cu—In—Ga—Se—O Multicomponent Chemistries 89
- 4.2.2.1 Cu-In-Se Co-deposition 89
- 4.2.2.2 Cu-In-Ga-Se Co-deposition 91
- 4.2.2.3 Cu—In—Ga—O Co-deposition 92
- 4.2.2.4 Cu-In-Ga Co-deposition 93
- 4.2.3 Annealing Methods 93
- 4.2.4 Fabrication of Solar Cells 95
- 4.3 Electrodeposited $Cu_2ZnSn(Se,S)_4$ (CZTS) and Emerging Materials 97
- 4.3.1 Cu₂ZnSn(Se,S)₄ (CZTS) 97
- 4.4 From the Rotating Disk to the Paddle Cell as a Scale-up Platform *99*
- 4.4.1 Introduction to Scale-up 99
- 4.4.2 Entirely New Solution Agitation Method 100
- 4.4.3 The Paddle Agitation Technique Is More Readily Scalable 101
- 4.4.4 Electrical Contact Between the Thin Seed Layer and the Source of Current *103*
- 4.4.5 Previous Scale-up of the Paddle Cell 103
- 4.4.6 Scale-up of the Paddle Cell to 15 cm × 15 cm 104
- 4.4.7 Scale-up of the Paddle Cell to $30 \text{ cm} \times 60 \text{ cm}$ 107
- 4.4.8 Improving Within-Wafer Uniformity, Reproducibility, and Demonstration of Scalability *108*
- 4.4.8.1 Within-Wafer Uniformity 108
- 4.4.8.2 Wafer-to-Wafer Reproducibility 109
- 4.5 Scaling-up to 60 cm × 120 cm from Tiny Electrodes to Meters *110*
- 4.5.1 A 1 m² min⁻¹ Continuous Industrial Scale 110
- 4.5.2 Bath Control 116
- 4.5.2.1 Insoluble Anode 118
- 4.5.2.2 Soluble Anode *118*
- 4.5.2.3 Bath Maintenance and Reproducibility and Steady-State Operation *119*
- 4.6 Conclusions 121 Acknowledgments 122 References 123

5 Thin-film Head and the Innovator's Dilemma 129 Keishi Ohashi

- 5.1 Introduction 129
- 5.2 Thin-film Head Technology 130
- 5.2.1 Magnetic Properties for HDD 130
- 5.2.2 Permalloy 130
- 5.2.3 Thin-film Head 132
- 5.2.4 Magnetic Domain Noise 133
- 5.3 Data Storage Business in Japan 137

- 5.3.1 Magnetic Thin-films for HDD in the 1980s 137
- 5.3.2 Use of Optics *138*
- 5.3.3 High-Moment Head Core Material 138
- 5.3.4 High-M_s Write Heads 141
- 5.4 The Innovator's Dilemma 142
- 5.4.1 Thin-film Head is not Disruptive 142
- 5.4.2 Small HDD *143*
- 5.4.3 MR Head 144
- 5.4.4 GMR Head 145
- 5.5 TMR Head 147
- 5.5.1 Infinite MR Ratio 147
- 5.5.2 Suspicions Surrounding the TMR Head 147
- 5.5.3 Low-Resistance TMR Head 148
- 5.5.4 MGO: The Final Push 150
- 5.5.5 Exploring New Markets 151
- 5.6 Discussion 151 Acknowledgments 152 References 153

6 Development of Fully-Continuous Electrokinetic Dewatering of Phosphatic Clay Suspensions 159

Rui Kong, Arthur Dizon, Saeed Moghaddam, and Mark E. Orazem

- 6.1 Introduction 159
- 6.1.1 Phosphatic Clay Suspensions 160
- 6.1.2 Industrial Scope 160
- 6.1.3 Why is Separation of Water from Clay Difficult? 161
- 6.2 Current Methods *162*
- 6.2.1 Flocculation 162
- 6.2.2 Mechanical Dewatering 163
- 6.2.3 Electrokinetic Separation 163
- 6.3 Development of Dewatering Technologies for Phosphatic Clays *164*
- 6.3.1 Lab-scale Batch Dewatering 165
- 6.3.2 Semi-continuous Operation to Recover Clear Supernatant 168
- 6.3.3 Semi-continuous Operation to Recover Solids 170
- 6.3.4 Continuous Operation *172*
- 6.3.5 Energy and Power Requirements for All Prototypes Tested 175
- 6.4 Economic Assessment for On-site Implementation 179
- 6.4.1 Hydrogen Emission 179
- 6.4.2 Capital and Operation Costs 180
- 6.4.2.1 Power and Energy consumption for On-site Operations 181
- 6.4.2.2 Operation cost 181
- 6.4.2.3 Capital Cost 183
- 6.4.3 Results 184
- 6.5 Our Next Prototype: Dual-zone Continuous Operation 185
- 6.6 Conclusions 186 Acknowledgments 187 References 187

Contents ix

7 Breaking the Chemical Paradigm in Electrochemical Engineering: Case Studies and Lessons Learned from Plating to Polishing 193

E. Jennings Taylor, Maria E. Inman, Holly M. Garich, Heather A. McCrabb, Stephen T. Snyder, and Timothy D. Hall

- 7.1 Introduction 193
- 7.1.1 Perspective 194
- 7.2 A Brief Overview of Pulse Reverse Current Plating 196
- 7.2.1 Mass Transport Effects in Pulse Current Plating 198
- 7.2.2 Current Distribution Effects in Pulse Current Plating 200
- 7.2.3 Grain Size Effects in Pulse Current Plating 204
- 7.2.4 Current Efficiency Effects in Pulse Current Plating 205
- 7.2.5 Concluding Remarks for Pulse Current Plating 205
- 7.3 Early Developments in Pulse Plating 206
- 7.3.1 Leveling Without Levelers Using Pulse Reverse Current Plating 207
- 7.3.2 Ductility Without Brighteners Using Pulse Current Plating 210
- 7.4 Transition of Pulse Current Plating Concepts to Surface Finishing *211*
- 7.4.1 Pulse Voltage Deburring of Automotive Planetary Gears 212
- 7.4.2 Transition to Pulse Reverse Voltage Electropolishing of Passive Materials *214*
- 7.4.3 Sequenced Pulse Reverse Voltage Electropolishing of Semiconductor Valves 216
- 7.4.4 Pulse Reverse Voltage Electropolishing of Strongly Passive Materials 220
- 7.4.5 Pulse Reverse Voltage Electropolishing of Niobium Superconducting Radio Frequency Cavities 223
- 7.4.6 Transition Pulse Reverse Voltage Electropolishing to Niobium Superconducting Radio Frequency Cavities 226
- 7.5 Concluding Thoughts 232 Acknowledgments 233 References 234
- 8 The Interaction Between a Proton and the Atomic Network in Amorphous Silica Glass Made a Highly Sensitive Trace Moisture Sensor 241

Yusuke Tsukahara, Nobuo Takeda, Kazushi Yamanaka, and Shingo Akao

- 8.1 Unexpected Long Propagation of Surface Acoustic Waves Around a Sphere 241
- 8.2 Invention of a Ball SAW Device and Application to Gas Sensors 243
- 8.3 Unexpected Fluctuations in the Output Signal of the Gas Sensor Leading to the Development of Trace Moisture Sensors 249
- 8.4 Sol–Gel Silica Film for the Trace Moisture Sensors 253
- 8.5 A Thermodynamic Model of Interaction of Water Vapor with Amorphous Silica Glass 254
- 8.6 Concluding Remarks 257 References 257

x Contents

9	From Sensors to Low-cost Instruments to Networks: Semiconducting Oxides as Gas-Sensitive Resistors 261
	David E. Williams
9.1	Overview 261
9.2	Basic Science of Semiconducting Oxides as Gas-Sensitive
	Resistors 266
9.2.1	Multiscale Modeling of Gas-Sensitive Resistors 266
9.2.1.1	Introduction 266
9.2.1.2	Effective Medium Model 1: Rationalization of Composition Effects on Response 268
9.2.1.3	Effective Medium Model 2: Diffusion-Reaction Effects on Response;
	Effects of Electrode Geometry and "Self-Diagnostic" Devices 270
9.2.1.4	Microstructure Model: Percolation and Equivalent Circuit
	Representation 277
9.2.2	Surface Segregation and Surface Modification Effects 284
9.2.2.1	Surface Modification by "Poisoning" 284
9.2.2.2	Surface Modification by Segregation 286
9.2.2.3	Surface Grafting as a Means for Altering Response 288
9.2.3	Surface Defect and Reaction Models 288
9.3	Commercial Development of Sensors and Instruments 291
9.3.1	Introduction 291
9.3.2	Development of a Low-Cost Instrument for Measurement of
	Ozone in the Atmosphere 298
9.3.3	Signal Drift Detection 303
9.3.4	A Low-Cost Instrument for Measurement of Atmospheric
	Nitrogen Dioxide 304
9.3.5	Networks of Instruments in the Atmosphere 306
9.4	Conclusion and Prospects 311
	Acknowledgment 313
	References 314
	Index 323