Contents

Preface *xi*

1 Application of Mössbauer Spectroscopy to Energy Materials *1*
Pierre-Emmanuel Lippens, Jean-Claude Jumas, and Josette Olivier-Fourcade
1.1 Introduction *1*
1.2 Mössbauer Spectroscopy for Li-ion and Na-ion Batteries *2*
1.2.1 Characterization of Electrode Materials and Electrochemical Reactions *2*
1.2.2 Tin-Based Negative Electrode Materials for Li-ion Batteries *3*
1.2.2.1 Electrochemical Reactions of Lithium with Tin *3*
1.2.2.2 Tin Oxides *7*
1.2.2.3 Tin Borophosphates *10*
1.2.2.4 Tin-Based Intermetallics *13*
1.2.3 Iron-Based Electrode Materials *17*
1.2.3.1 $LiFePO_4$ as Positive Electrode Material for Li-ion Batteries *17*
1.2.3.2 $Fe_{1.19}PO_4(OH)_{0.57}(H_2O)_{0.43}$/C as Positive Electrode Material for Li-ion Batteries *18*
1.2.3.3 $Na_{1.5}Fe_{0.5}Ti_{1.5}(PO_4)_3$/C as Electrode Material for Na-ion Batteries *19*
1.3 Mössbauer Spectroscopy of Tin-Based Catalysts *21*
1.3.1 Reforming Catalysis *21*
1.3.2 Redox Properties of Pt-Sn Based Catalysts *22*
1.3.3 Trimetallic Pt-Sn-In Based Catalysts *24*
1.4 Conclusion *26*
Acknowledgments *27*
References *27*

2 Mössbauer Spectral Studies of Iron Phosphate Containing Minerals and Compounds *33*
Gary J. Long and Fernande Grandjean
2.1 Introduction *33*
2.2 Thermodynamic Properties of Iron Phosphate Containing Compounds *34*

2.3 Room Temperature Mössbauer Spectra of Iron Phosphate Containing Minerals *37*
2.4 Analysis of Magnetically Ordered Mössbauer Spectra *50*
2.5 Structural and Thermodynamic Properties of the Polymorphs of $FePO_4$ *53*
2.5.1 Polymorphs of $FePO_4$ *53*
2.6 Mössbauer Spectra of α-$FePO_4$ *55*
2.7 Magnetic Structure of α-$FePO_4$, Obtained by Mössbauer Spectroscopy *57*
2.7.1 Magnetic Structure of α-$FePO_4$ *57*
2.8 Temperature Dependence of the α-$FePO_4$ Structure Tilt Angle *60*
2.9 Mössbauer Spectral Studies on Metastable Polymorphs of $FePO_4$ *62*
2.9.1 Crystallographic Structures of Two Polymorphs of $FePO_4 \cdot 2H_2O$ *62*
2.9.2 Preparation and Crystallographic Structures of the Two Polymorphs, γ-$FePO_4$ and ζ-$FePO_4$ *62*
2.9.3 Mössbauer Spectral Studies of $FePO_4$ Metastable Polymorphs *64*
2.9.4 Preparation and Mössbauer Spectra of Synthetic Heterosite, $(Fe,Mn)PO_4$ *67*
2.9.5 Fits of the Magnetic Mössbauer Spectra of η-$Fe_{0.9}Mn_{0.1}PO_4$ *68*
2.10 Mössbauer Spectral Studies of Various Iron Phosphate Compounds *73*
2.10.1 Mössbauer Spectral Properties of α-$Fe_2(PO_4)O$ *74*
2.10.2 Mössbauer Spectral Properties of $Fe_3(PO_4)O_3$ *79*
2.10.3 Preparation and Structural Properties of $Fe_9(PO_4)O_8$ *80*
2.10.4 Mössbauer Spectral Properties of $Fe_9(PO_4)O_8$ *81*
Acknowledgments *85*
References and Notes *85*

3 Mössbauer Spectroscopic Investigation of Fe-Based Silicides *93*
Xiao Chen, Junhu Wang, and Changhai Liang
3.1 Introduction *93*
3.2 Mössbauer Spectroscopic Investigation of Iron Silicides Prepared By Mechanical Alloying and Heat Treatment *95*
3.3 Mössbauer Spectra of Iron Silicide on Silica Prepared by Pyrolysis of Ferrocene-Polydimethylsilane Composites *99*
3.4 Synthesis and Mössbauer Spectra of Iron Silicides by Temperature-Programmed Silicification *102*
3.5 Mössbauer Spectroscopic Investigation of Doped Iron Silicides *104*
3.6 Conclusion and Perspective *107*
References *108*

4 Mössbauer Spectroscopy of Catalysts *113*
Károly Lázár
4.1 Introduction *113*
4.2 Principles of the Mössbauer Effect and Outlook of Its Application for Catalyst Studies *116*

4.2.1 Brief Overview of the Basics of Mössbauer Spectroscopy *116*
4.2.2 Mössbauer Spectroscopy from the Point of View of Catalyst Studies – Particular Features *117*
4.2.3 The Probability of the Mössbauer Effect – f-Factor and Size Effects *118*
4.2.4 Variants of the Technique *120*
4.2.4.1 ^{57}Co Emission Spectroscopy *120*
4.2.4.2 Synchrotron-Based NFS (Nuclear Forward Scattering) *122*
4.2.4.3 Conversion Electron Mössbauer Spectroscopy *122*
4.2.5 Technical Implementations – Experimental Conditions *123*
4.3 Heterogeneous Catalysts *124*
4.3.1 Sites on Supported Particles with Different Participation in Catalytic Processes *124*
4.3.2 Collective Effects in Particles (Magnetism) *125*
4.3.3 Case Studies *126*
4.3.3.1 Metals and Alloys *126*
4.3.3.2 Oxide Catalysts *130*
4.3.3.3 Catalysts with Fe–N, Fe–C, and Fe–N–C Centers *133*
4.4 Biocatalysts – Enzymes *135*
4.5 Homogeneous Catalysts – Frozen Solutions *135*
4.5.1 Studies on Reaction Intermediates – Time-Resolved Freeze-Quenched Spectra *136*
4.6 Conclusions *137*
Acknowledgment *137*
References *138*

5 Application of Mössbauer Spectroscopy in Studying Catalysts for CO Oxidation and Preferential Oxidation of CO in H_2 *145*
Kuo Liu, Junhu Wang, and Tao Zhang
5.1 Introduction *145*
5.2 Application of Mössbauer Spectroscopy in CO Oxidation *147*
5.2.1 ^{57}Fe Mössbauer Spectroscopy *147*
5.2.2 ^{119}Sn Mössbauer Spectroscopy *150*
5.2.3 ^{197}Au Mössbauer Spectroscopy *151*
5.2.4 ^{193}Ir Mössbauer spectroscopy *152*
5.3 Application of Mössbauer Spectroscopy in PROX *153*
5.3.1 PtFe-Containing Catalysts *153*
5.3.2 Au-Based Catalysts *155*
5.3.3 IrFe-Containing Catalysts *158*
5.3.3.1 Porous Carbon Supported IrFe Catalysts *158*
5.3.3.2 SiO_2 and Al_2O_3 Supported IrFe Catalysts *159*
5.3.4 CuO/CeO_2 with Fe_2O_3 Additive *165*
5.4 Concluding Remarks *165*
Acknowledgments *166*
References *166*

6 Application of ^{57}Fe Mössbauer Spectroscopy in Studying Fe–N–C Catalysts for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells *171*
Xinlong Xu, Junhu Wang, Suli Wang, and Gongquan Sun
6.1 Introduction *171*
6.2 Advanced ^{57}Fe Mössbauer Spectroscopy Technique *173*
6.2.1 Room Temperature ^{57}Fe Mössbauer Spectroscopy *173*
6.2.2 Low Temperature and Computational ^{57}Fe Mössbauer Spectroscopy *174*
6.2.3 In Situ Electrochemical ^{57}Fe Mössbauer Spectroscopy *175*
6.3 Characterization of Fe–N–C Using ^{57}Fe Mössbauer Spectroscopy *177*
6.3.1 Identification of Active Sites *177*
6.3.2 Investigation of Degradation Mechanism *180*
6.3.3 Optimization for Synthesis of Fe–N–C *184*
6.3.3.1 Precursor Composition *184*
6.3.3.2 Heat Treatment *185*
6.4 Summary and Perspective *187*
Acknowledgments *188*
References *188*

7 ^{197}Au Mössbauer Spectroscopy of Thiolate-protected Gold Clusters *195*
Norimichi Kojima, Yasuhiro Kobaqyashi, and Makoto Seto
7.1 Introduction *195*
7.2 Synthesis of Thiolate Protected Gold Clusters *197*
7.3 ^{197}Au Mössbauer Spectroscopy of Gold Nano-clusters *198*
7.3.1 Experimental Procedure of ^{197}Au Mössbauer Spectroscopy *198*
7.3.2 ^{197}Au Mössbauer Spectra of $Au_n(SG)_m$ ($n = 10\sim55$) *198*
7.3.3 Molecular Structure and ^{197}Au Mössbauer Spectra of $Au_{10}(SG)_{10}$ *198*
7.3.4 Molecular Structure and ^{197}Au Mössbauer Spectra of $Au_{25}(SG)_{18}$ *200*
7.3.5 Structural Evolution of $Au_n(SG)_m$ ($n = 10\sim55$) Based on ^{197}Au Mössbauer Spectroscopy *201*
7.3.6 ^{197}Au Mössbauer Spectra of $Au_{24}Pd_1(SC_{12}H_{25})_{18}$ *204*
7.3.7 ^{197}Au Mössbauer Spectra of $Au_n(SC_{12}H_{25})_m$ *205*
7.4 Conclusion *208*
Acknowledgments *208*
References *209*

8 ^{197}Au Mössbauer Spectroscopy of Gold Mixed-Valence Complexes, $Cs_2[Au^IX_2][Au^{III}Y_4]$(X, Y = Cl, Br, I) and $[NH_3(CH_2)_nNH_3]_2[(Au^II_2)(Au^{III}I_4)(I_3)_2]$ (n = 7, 8) *213*
Norimichi Kojima, Yasuhiro Kobaqyashi, and Makoto Seto
8.1 Introduction *213*
8.2 Experimental Procedure *216*
8.2.1 Synthesis and Characterization *216*

8.2.1.1 $Cs_2[Au^IX_2][Au^{III}Y_4]$ (X, Y = Cl, Br, I) *216*
8.2.1.2 $[NH_3(CH_2)_nNH_3]_2[(Au^II_2)(Au^{III}I_4)(I_3)_2]$ (n = 7, 8) *217*
8.2.2 ^{197}Au Mössbauer Spectroscopy *217*
8.3 Crystal Structure of $Cs_2[Au^IX_2][Au^{III}Y_4]$ (X, Y = Cl, Br, I) *218*
8.4 Chemical Bond of Au–X in $[Au^IX_2]^-$ and $[Au^{III}X_4]^-$ *221*
8.5 Mössbauer Parameters of ^{197}Au in $[Au^IX_2]^-$ and $[Au^{III}X_4]^-$ *223*
8.5.1 Mössbauer Parameters of ^{197}Au in $(C_4H_9)_4N[Au^IX_2]$ and $(C_4H_9)_4N[Au^{III}X_4]$ *224*
8.5.1.1 Isomer Shift *224*
8.5.1.2 Quadrupole Splitting *224*
8.5.2 Mössbauer Parameters of ^{197}Au in $Cs_2[Au^IX_2][Au^{III}X_4]$ (X = Cl, Br, I) *225*
8.5.2.1 Isomer Shift *225*
8.5.2.2 Quadrupole Splitting *226*
8.5.2.3 Analysis of ^{197}Au Mössbauer Parameters for $Cs_2[Au^IX_2][Au^{III}X_4]$ *226*
8.6 Charge Transfer Interaction in $Cs_2[Au^IX_2][Au^{III}X_4]$ (X = Cl, Br, I) *227*
8.7 ^{197}Au Mössbauer Spectra of $Cs_2[Au^IX_2][Au^{III}Y_4]$ (X, Y = Cl, Br, I) *228*
8.7.1 Isomer Shift of Au^I in $Cs_2[Au^IX_2][Au^{III}Y_4]$ *228*
8.7.2 Isomer Shift of Au^{III} in $Cs_2[Au^IX_2][Au^{III}Y_4]$ *230*
8.7.3 Quadrupole Splitting of Au^I in $Cs_2[Au^IX_2][Au^{III}Y_4]$ *230*
8.7.4 Quadrupole Splitting of Au^{III} in $Cs_2[Au^IX_2][Au^{III}Y_4]$ *231*
8.8 Single Crystal ^{197}Au Mössbauer Spectra of $Cs_2[Au^II_2][Au^{III}I_4]$ *231*
8.8.1 Comparison of ^{197}Au Mössbauer Spectra Between Single Crystal and Powder Crystal *231*
8.8.2 Sign of EFG for Au^I in $[Au^II_2]^-$ and Au^{III} in $[Au^{III}X_4]^-$ *234*
8.9 ^{197}Au Mössbauer Spectra of $Cs_2[Au^IX_2][Au^{III}X_4]$ (X = Cl, I) Under High Pressures *235*
8.9.1 Phase Diagram of $Cs_2[Au^IX_2][Au^{III}X_4]$ (X = Cl, Br, I) *235*
8.9.2 Origin of Metallic Mixed-Valence State in $Cs_2[Au^ICl_2][Au^{III}Cl_4]$ *236*
8.9.3 Au Valence Transition in $Cs_2[Au^II_2][Au^{III}I_4]$ *239*
8.10 ^{197}Au Mössbauer Spectra of $[NH_3(CH_2)_nNH_3]_2$ $[(Au^II_2)(Au^{III}I_4)(I_3)_2]$ (n = 7, 8) *241*
8.11 Conclusion *243*
Acknowledgments *244*
References *245*

9 Temperature- and Photo-Induced Spin-Crossover in Molecule-Based Magnets *251*
Hiroko Tokoro, Kenta Imoto, and Shin-ichi Ohkoshi
9.1 Introduction *251*
9.2 Spin-Crossover Phenomena in Cesium Iron Hexacyanidochromate Prussian Blue Analog *252*
9.3 Light-Induced Spin-Crossover Magnet in Iron Octacyanidoniobate Bimetal Assembly *254*

9.4 Chiral Photomagnetism and Light-Controllable Second Harmonic Light in Iron Octacyanidoniobate Bimetal Assembly *258*
9.5 Conclusion and Perspective *265*
References *265*

10 Developing a Methodology to Obtain New Photoswitchable Fe(II) Spin Crossover Complexes *271*
Varun Kumar and Yann Garcia
10.1 Introduction and Context *271*
10.2 Introduction to a New Photo-responsive Anion: *psca* *275*
10.3 Combining Fe(II) and *psca* Together in a Single Compound *276*
10.4 Fe(II) Mononuclear Complexes with DMPP and *psca* Ligands *278*
10.5 1D Fe(II) Coordination Polymer with *psca* as Non-Coordinated Anions *281*
10.6 Conclusions and Perspectives *284*
References *285*

11 ^{57}Fe Mössbauer Spectroscopy as a Prime Tool to Explore a New Family of Colorimetric Sensors *291*
Li Sun, Weiyang Li, and Yann Garcia
11.1 Introduction and General Context *291*
11.2 Colorimetric Gas Sensors Based on Fe(II) Complexes *292*
11.3 Conclusions and Perspectives *306*
References *306*

Index *311*