
Molten Salts and Ionic Liquids 18

Editors:

W. M. Reichert

University of South Alabama
Mobile, Alabama, USA

R. A. Mantz

U.S. Army Research Office
Durham, North Carolina, USA

P. C. Trulove

U.S. Naval Academy
Annapolis, Maryland, USA

A. Ispas

Technische Universität Ilmenau
Thuringia, Germany

D. M. Fox

American University
Washington, DC, USA

M. Mizuhata

Kobe University
Hyōgo, Japan

H. C. De Long

Air Force Office of Scientific Research
Arlington, Virginia, USA

A. Bund

Technische Universität Ilmenau
Thuringia, Germany

Sponsoring Divisions:



Physical and Analytical Electrochemistry



Electrodeposition



Energy Technology



Published by

The Electrochemical Society

65 South Main Street, Building D
Pennington, NJ 08534-2839, USA

tel 609 737 1902

fax 609 737 2743

www.electrochem.org

ecstransactions™

Vol. 50, No. 11

Copyright 2012 by The Electrochemical Society.
All rights reserved.

This book has been registered with Copyright Clearance Center.
For further information, please contact the Copyright Clearance Center,
Salem, Massachusetts.

Published by:

The Electrochemical Society
65 South Main Street
Pennington, New Jersey 08534-2839, USA

Telephone 609.737.1902
Fax 609.737.2743
e-mail: ecs@electrochem.org
Web: www.electrochem.org

ISSN 1938-6737 (online)
ISSN 1938-5862 (print)
ISSN 2151-2051 (cd-rom)

ISBN 978-1-62332-010-2 (Hardcover)
ISBN 978-1-60768-359-9 (PDF)

Printed in the United States of America.

Table of Contents

Preface *iii*

Chapter 1 Max Bredig Award Address

(Max Bredig Award in Molten Salt and Ionic Liquid Chemistry) Exploring Novel Uses of Molten Salts 3
D. Fray

Chapter 2 Extractive Metallurgy

Behaviour of Cr Species in the Molten System NaF - AlF₃ - (Al₂O₃) 17
V. Danielik, P. Fellner, D. Šuleková, and J. Thonstad

Electrochemical Near-Net-Shape Production Via the FFC Cambridge Process --- Dedication to the Special Session for the 2012 Max Bredig Award 29
D. Hu and G. Z. Chen

Deoxidation of Titania Foams 39
E. Krasicka-Cydzik

Synchrotron X-ray Diffraction Monitoring of the Operation of an Inert Anode Utilized in a Cambridge FFC-Cell 45
G. A. Snook, M. R. Rowles, M. J. Styles, K. McGregor, I. C. Madsen, A. J. Urban, N. V. Scarlett, and D. P. Riley

Room Temperature Ionic Liquid as Electrolyte for Lithium-Ion Battery 57
Y. Fung, Y. Yang, J. Zheng, and D. Zhu

Chapter 3

Electrochemistry in Molten Salts and Ionic Liquids

An Arrhenius Argument to Explain Electrical Conductivity Maxima Versus Temperature <i>C. M. Kuntz and A. L. East</i>	71
Electrochemical Investigation of Quinone Complexation by Lewis Acids in a Chloroaluminate Ionic Liquid <i>G. T. Cheek</i>	79
Effects of the Charge Density of the Anions of Ionic Liquids on the Electrode Kinetics of Ruthenium 2,2'-Bipyridine Complexes <i>Y. Katayama, Y. Toshimitsu, and T. Miura</i>	87
Voltammetric Studies of Proton Reduction in 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate <i>G. T. Cheek, D. F. Roeper, and W. E. O'Grady</i>	97
Robust Microelectrodes In Molten Salt Analysis <i>A. Relf, D. Corrigan, C. L. Brady, J. G. Terry, A. J. Walton, and A. R. Mount</i>	105
PTFE Bound Activated Carbon - A Quasi Reference Electrode for Ionic Liquids and Its Application <i>D. Weingarh, A. Foelske-Schmitz, A. Wokaun, and R. Kötz</i>	111
Fundamental Study on Reduction Rate for Electrolytic Reduction of SiO ₂ Powder in Molten CaCl ₂ <i>T. Toba, K. Yasuda, T. Nohira, R. Hagiwara, K. Ichitsubo, K. Masuda, and T. Homma</i>	119
Anodic Reactions on Some Materials in LiCl-KCl Melt <i>T. Takenaka, M. Umehara, D. Araki, and T. Morishige</i>	127
Effect of the Second Coordination Sphere on the Standard Rate Constants of Charge Transfer for the Cr(III)/Cr(II) Redox Couple in Chloride Melts <i>Y. V. Stulov, V. G. Kremenetsky, and S. A. Kuznetsov</i>	135
Electrochemical Behavior of Vanadium Oxides in (NH ₂) ₂ CO - KCl Melt <i>A. V. Savchuk and S. V. Devyatkin</i>	153
Electrode Kinetics of Oxygen/Superoxide Ion Redox Couple in Some Amide-Type Ionic Liquids <i>T. Nakagawa, Y. Katayama, and T. Miura</i>	159

Reaction Entropies of Some Redox Couples in Ionic Liquids <i>Y. Yamato, Y. Katayama, and T. Miura</i>	167
Electrochemical Behavior of Bis(Trifluoromethylsulfonyl)Imide-Based ILs at Gold Single Crystal Electrodes <i>H. Ueda, K. Nishiyama, and S. Yoshimoto</i>	175
Electrochemical Behavior and Electrorefining of Vanadium in Melts Containing Titanium Salts <i>O. S. Kazakova and S. A. Kuznetsov</i>	181
Electrode Reactions of Platinum Bromide Complexes in an Amide-Type Ionic Liquid <i>T. Endo, Y. Katayama, and T. Miura</i>	191
Electrochemical Polishing Applications and EIS of a Novel Choline Chloride-Based Ionic Liquid <i>A. I. Wixtrom, J. E. Buhler, C. E. Reece, and T. M. Abdel-Fattah</i>	199

Chapter 4 **Electrodeposition in Molten Salts and Ionic Liquids**

Recent Developments in Low-Temperature Electrolysis of Aluminum <i>A. Redkin, A. Apisarov, A. Dedyukhin, V. Kovrov, Y. Zaikov, O. Tkacheva, and J. Hryn</i>	205
Electrodeposition of Lead from Chloride Melts <i>G. Haarberg, L. Owe, B. Qin, J. Wang, and R. Tunold</i>	215
Electrodeposition on Tantalum in Alkali Halide Melts <i>J. H. von Barner, A. H. Jensen, and E. Christensen</i>	221
Electrochemical Deposition of Niobium onto the Surface of Copper Using a Novel Choline Chloride-Based Ionic Liquid <i>A. I. Wixtrom, J. E. Buhler, C. E. Reece, and T. M. Abdel-Fattah</i>	225
Ta and Nb Electrodeposition from Ionic Liquids <i>S. Krischok, A. Ispas, A. Zühlsdorff, A. Ulbrich, A. Bund, and F. Endres</i>	229
Al-W Alloy Deposition from Lewis Acidic Room-Temperature Chloroaluminate Ionic Liquid <i>T. Tsuda, Y. Ikeda, T. Arimura, A. Imanishi, S. Kuwabata, C. L. Hussey, and G. Stafford</i>	239

An Inverted Aluminum Electrolysis Cell Using a High Density Electrolyte and an Inert Anode - A Test of the Concept <i>S. Rolseth, H. Gudbrandsen, and J. Thonstad</i>	251
Complex Formation and Micropassivation at Electrodeposition of Niobium Coatings in Alkali Chloride-Fluoride Melts with Different Cationic Composition <i>E. A. Marenkova and S. A. Kuznetsov</i>	263
Electrochemical Deposition of Cobalt onto the Surface of Copper Using a Choline Chloride-Based Ionic Liquid <i>B. T. Damiano, A. Shenenberger, A. I. Wixtrom, and T. M. Abdel-Fattah</i>	277

Chapter 5

New Molten Salts and Ionic Liquids and Their Properties

(Keynote) Protic Ionic Liquids Based on a Super-Strong Acid: Bulk and Electrochemical Properties <i>M. Miran, T. Yasuda, M. Susan, K. Dokko, and M. Watanabe</i>	285
(Keynote) Boronium Based Ionic Liquids: Salts of Boron Centered Cations as Promising Salts for Electrochemical Applications <i>J. H. Davis Jr., T. Ruether, and S. C. Dorman</i>	293
(Keynote) Theoretical Deconstruction of the X-ray Structure Function Exposes Polarity Alternations in Room Temperature Ionic Liquids <i>H. Kashyap and C. J. Margulis</i>	301
Physicochemical and Electrochemical Properties of Novel Ionic Liquids Containing Aprotic Heterocyclic Anions Doped with Lithium Salts <i>C. Shi, M. Quiroz-Guzman, A. DeSilva, and J. Brennecke</i>	309
Electronic Absorption Spectra of Niobium Species in Halide Melts <i>N. Brevnova, I. B. Polovov, M. Chernyshov, V. A. Volkovich, B. Vasin, and T. Griffiths</i>	325
Hysteresis Effects in the In Situ SFG and Differential Capacitance Measurements on Metal Electrode/Ionic Liquids Interface <i>W. Zhou, Y. Xu, and Y. Ouchi</i>	339
Visualization of Ionic-Liquid/Solid Interfaces by Frequency Modulation Atomic Force Microscopy <i>M. Negami, T. Ichii, K. Murase, and H. Sugimura</i>	349

Corrosion of Nickel-Chromium-Molybdenum Based Alloy in Chloride Melts Containing Transition Metal Ions 357
A. Abramov, V. Karpov, I. B. Polovov, D. Vinogradov, V. A. Volkovich, and O. Rebrin

Influence of the Second Coordination Sphere on the Diffusion Coefficients of Niobium Fluoride Complexes in Chloride and Fluoride Melts 367
A. V. Popova, V. G. Kremenetsky, and S. A. Kuznetsov

Chapter 6 Power and Energy Applications

Towards Li-Air and Li-S Batteries: Understanding the Morphological Changes of Lithium Surfaces during Cycling at a Range of Current Densities in an Ionic Liquid Electrolyte 383
A. I. Bhatt, P. Kao, A. S. Best, and A. F. Hollenkamp

Oxygen Reduction Reaction at LaNiO₃ Supported by Au Ring in Li/Na Eutectic Carbonate with La₂O₃ 403
K. Matsuzawa, Y. Esaki, Y. Takeuchi, K. Watanabe, Y. Kohno, K. Ota, and S. Mitsushima

EMIHSO₄-Based Polymer Electrolytes and Their Applications in Solid Electrochemical Capacitors 411
S. Ketabi, X. Liu, Z. Le, and K. Lian

Influence of Nonflammable Diluents on Properties of Phosphonium Ionic Liquids as Lithium Battery Electrolytes 419
K. Tsunashima, H. Taguchi, and F. Yonekawa

Chapter 7 Separations and Purification

(Keynote) Exploiting the Versatility of Ionic Liquids and Polymeric Ionic Liquids in Chromatographic Separations and Microextractions 427
T. D. Ho, M. D. Joshi, H. Yu, P. Twu, T. Li, W. Cole, and J. L. Anderson

(Keynote) Separation of Flue Gas Components by SILP (Supported Ionic Liquid-Phase) Absorbers 433
P. L. Thomassen, A. J. Kunov-Kruse, S. L. Mossin, H. Kolding, S. Kegnaes, A. Riisager, and R. Fehrmann

Decomposition of CO₂ Gas in CaCl₂-CaO and LiCl-Li₂O Molten Salts 443
R. O. Suzuki, K. Otake, T. Uchiyama, H. Kinoshita, N. Sakaguchi, and T. Kikuchi

Chapter 8
Rare Earth and Nuclear Chemistry

Extraction of Rare Earth Metals from Nd-based Scrap by Electrolysis from Molten Salts <i>A. Martinez, O. Kjos, E. Skybakmoen, A. Solheim, and G. Haarberg</i>	453
(Keynote) Separation of Dy and Nd (La) Using Molten Salt and an Alloy Diaphragm <i>H. Konishi, H. Ono, T. Nohira, and T. Oishi</i>	463
Electrochemical Formation of RE-Ni (RE=Pr, Nd, Dy) Alloys in Molten Halides <i>T. Nohira, S. Kobayashi, K. Kondo, K. Yasuda, R. Hagiwara, T. Oishi, and H. Konishi</i>	473
Processing Al-Sc Alloys at Liquid Aluminum Cathode in KF-AlF ₃ Molten Salt <i>Q. Liu, J. Xue, J. Zhu, Y. Qian, and L. Feng</i>	483
Electrorefining of Zirconium from Zircaloy-4 Cladding Hulls in LiCl-KCl Molten Salts <i>C. Lee, K. Kang, M. Jeon, C. Heo, and Y. Lee</i>	491
Uranium Activity and Solubility in Liquid Ga-In Eutectic Alloy: An Electrochemistry Study <i>V. A. Volkovich, D. Maltsev, L. Yamshchikov, A. Osipenko, S. Raspopin, and M. Kormilitsyn</i>	497
Activity Coefficients and Solubility of Lanthanum and Praseodymium in Gallium-Indium Eutectic Alloy <i>A. Dedyukhin, V. Ivanov, S. Mel'chakov, A. Shchetinskii, V. A. Volkovich, L. Yamshchikov, A. Osipenko, S. Raspopin, and M. Kormilitsyn</i>	507
Precipitation of Rare Earth Phosphates from NaCl-2CsCl Eutectic Based Melts <i>V. A. Volkovich, A. Ivanov, S. Yakimov, I. B. Polovov, B. Vasin, T. Griffiths, A. Chukin, and A. Shtolts</i>	517
Investigation of Oxidation State of the Electrodeposited Neodymium Metal Related with the Water Content of Phosphonium Ionic Liquids <i>H. Kondo, M. Matsuniya, K. Tsunashima, and S. Kodama</i>	529
Electrochemical Behavior and Solvation Analysis of Rare Earth Complexes in Ionic Liquids Media Investigated by SECM and Raman Spectroscopy <i>N. Tsuda, M. Matsumiya, K. Tsunashima, and S. Kodama</i>	539
Development of Recycling Process for Rare Earth Magnets by Electrodeposition Using Ionic Liquids Media <i>M. Ishii, M. Matsumiya, and S. Kawakami</i>	549

Electrochemical Formation of Tb-Ni Alloys in a Molten LiCl-KCl-TbCl ₃ System <i>H. Konishi, K. Mizuma, H. Ono, E. Takeuchi, T. Nohira, and T. Oishi</i>	561
---	-----

Chapter 9 Biomass Applications

Polysaccharide Ecocomposite Materials: Synthesis, Characterization and Application for Removal of Pollutants and Bacteria <i>S. Duri, B. El-Zahab, and C. D. Tran</i>	573
Electrospinning of Biopolymers from Ionic Liquid - Co-Solvent Systems <i>E. K. Brown, L. M. Haverhals, M. P. Foley, H. De Long, and P. Trulove</i>	595
Ionic Liquid-based Solvents for Natural Fiber Welding <i>L. M. Haverhals, M. P. Foley, E. K. Brown, L. M. Nevin, D. M. Fox, H. De Long, and P. Trulove</i>	603
Formation of Surface Structures on Biopolymer Substrates Through the Inkjet Printing of Ionic Liquids <i>L. M. Haverhals, E. K. Brown, M. P. Foley, H. De Long, and P. Trulove</i>	615
Synthesis of Long Chain Brønsted Acidic Ionic Liquids <i>W. M. Reichert, A. Mirjafari, T. Goode, N. Williams, M. La, V. Ho, M. Yoder, and J. H. Davis Jr.</i>	623
Ionic Liquid Facilitated Introduction of Functional Materials into Biopolymer Polymer Substrates <i>L. M. Haverhals, W. M. Reichert, S. Nazare, M. Zammarano, J. W. Gilman, H. De Long, and P. Trulove</i>	631

Chapter 10 Materials

Cyclic Voltammetry and XAS Studies of Transition Metal Chlorides in the Ionic Liquid 1-Ethyl-3-Methyl Imidazolium Chloride/ Aluminum Chloride <i>D. F. Roeper, G. T. Cheek, K. I. Pandya, and W. E. O'Grady</i>	643
Intercalation Chemistry of Ionic Liquids <i>T. E. Sutto and T. T. Duncan</i>	655
Dispersion of Organically Modified Layered Silicates in Melt Blended Poly(Lactic Acid) Composites: Effects of Cation Head Groups and Oxygenated Alkyl Chains <i>D. M. Fox, M. Zammarano, M. Novy, L. M. Haverhals, H. De Long, and P. Trulove</i>	665

Molten Salts as a Promising Medium for the Synthesis of Highly Active Catalytic Coatings	677
<i>A. R. Dubrovskiy and S. A. Kuznetsov</i>	
Corrosion of Austenitic Steels and Their Components in Vanadium-Containing Chloride Melts	685
<i>A. Abramov, I. B. Polovov, V. A. Volkovich, O. Rebrin, E. Denisov, and T. Griffiths</i>	
Corrosion of Ferritic and Ferritic-Martensitic Steels in NaCl-KCl-VCl ₂ Melts	699
<i>I. B. Polovov, D. Vinogradov, A. Abramov, A. Shak, V. A. Volkovich, O. Rebrin, and T. Griffiths</i>	
Synthesis of Refractory Metal Carbide Nanocoatings on Carbon Fibers and Nanoneedles of Silicon in Molten Salts	711
<i>V. S. Dolmatov and S. A. Kuznetsov</i>	
Author Index	717