

Electrodeposition from Ionic Liquids

Edited by
Frank Endres, Douglas MacFarlane,
and Andrew Abbott



WILEY-VCH Verlag GmbH & Co. KGaA

Electrodeposition from Ionic Liquids

Edited by

*Frank Endres, Douglas MacFarlane,
and Andrew Abbott*

Related Titles

Wasserscheid, P., Welton, T. (eds.)

Ionic Liquids in Synthesis

2007

ISBN 978-3-527-31239-9

Staikov, G. T. (ed.)

Electrocrystallization in Nanotechnology

2007

ISBN 978-3-527-31515-4

Paunovic, M., Schlesinger, M.

Fundamentals of Electrochemical Deposition

2006

ISBN 978-0-471-71221-3

Ohno, H.

Electrochemical Aspects of Ionic Liquids

2005

ISBN 978-0-471-64851-2

Electrodeposition from Ionic Liquids

Edited by
Frank Endres, Douglas MacFarlane,
and Andrew Abbott



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. Frank Endres

Faculty of Natural and Material Sciences
Clausthal University of Technology
38678 Clausthal-Zellerfeld
Germany

Prof. Douglas MacFarlane

School of Chemistry
Monash University
Clayton, Victoria 3800
Australia

Prof. Dr. Andrew Abbott

Chemistry Department
University of Leicester
Leicester LE1 7RH
United Kingdom

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Aptara, Inc., New Delhi, India

Printing Strauss GmbH, Mörlenbach

Bookbinding Litges & Dopf GmbH, Heppenheim

Cover Design Kessler, Karlsruhe

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN 978-3-527-31565-9

Contents

Preface IX

Foreword XIII

List of Contributors XV

List of Abbreviations XIX

- 1 Why use Ionic Liquids for Electrodeposition?** 1
Andrew P. Abbott, Ian Dalrymple, Frank Endres, and Douglas R. MacFarlane
 - 1.1 Non-aqueous Solutions 3
 - 1.2 Ionic Fluids 3
 - 1.3 What is an Ionic Liquid? 4
 - 1.4 Technological Potential of Ionic Liquids 6
 - 1.5 Concluding Remarks 12
 - References 12
- 2 Synthesis of Ionic Liquids** 15
Tom Beyersdorff, Thomas J. S. Schubert, Urs Welz-Biermann, Will Pitner, Andrew P. Abbott, Katy J. McKenzie, and Karl S. Ryder
 - 2.1 Synthesis of Chloroaluminate Ionic Liquids 15
 - 2.2 Air- and Water-stable Ionic Liquids 21
 - 2.3 Eutectic-based Ionic Liquids 31
 - References 42
- 3 Physical Properties of Ionic Liquids for Electrochemical Applications** 47
Hiroynuki Ohno
 - 3.1 Introduction 47
 - 3.2 Thermal Properties 47
 - 3.3 Viscosity 54
 - 3.4 Density 55
 - 3.5 Refractive Index 56
 - 3.6 Polarity 58
 - 3.7 Solubility of Metal Salts 64

3.8	Electrochemical Properties	66
3.9	Conclusion and Future Prospects	77
	Acknowledgement	77
	References	78
4	Electrodeposition of Metals	83
	<i>Thomas Schubert, Sherif Zein, El Abedin, Andrew P. Abbott, Katy J. McKenzie, Karl S. Ryder, and Frank Endres</i>	
4.1	Electrodeposition in AlCl_3 -based Ionic Liquids	84
4.2	Electrodeposition of Metals in Air- and Water-stable Ionic Liquids	92
4.3	Deposition of Metals from Non-chloroaluminate Eutectic Mixtures	103
4.4	Troublesome Aspects	114
	References	120
5	Electrodeposition of Alloys	125
	<i>I.-Wen Sun, and Po-Yu Chen</i>	
5.1	Introduction	125
5.2	Electrodeposition of Al-containing Alloys from Chloroaluminate Ionic Liquids	126
5.3	Electrodeposition of Zn-containing Alloys from Chlorozincate Ionic Liquids	132
5.4	Fabrication of a Porous Metal Surface by Electrochemical Alloying and De-alloying	137
5.5	Nb–Sn	139
5.6	Air- and Water-stable Ionic Liquids	140
5.7	Summary	145
	References	145
6	Electrodeposition of Semiconductors in Ionic Liquids	147
	<i>Natalia Borisenko, Sherif Zein El Abedin, and Frank Endres</i>	
6.1	Introduction	147
6.2	Gallium Arsenide	149
6.3	Indium Antimonide	149
6.4	Aluminum Antimonide	150
6.5	Zinc Telluride	150
6.6	Cadmium Telluride	151
6.7	Germanium	151
6.8	Silicon	155
6.9	Grey Selenium	160
6.10	Conclusions	164
	References	164
7	Conducting Polymers	167
	<i>Jennifer M. Pringle, Maria Forsyth, and Douglas R. MacFarlane</i>	
7.1	Introduction	167
7.2	Electropolymerization – General Experimental Techniques	171

7.3	Synthesis of Conducting Polymers	177
7.4	Characterization	191
7.5	Future Directions	203
7.6	Conclusions	207
	References	208
8	Nanostructured Metals and Alloys Deposited from Ionic Liquids	213
	<i>Rolf Hempelmann, and Harald Natter</i>	
8.1	Introduction	213
8.2	Pulsed Electrodeposition from Aqueous Electrolytes	215
8.3	Special Features of Ionic Liquids as Electrolytes	220
8.4	Nanocrystalline Metals and Alloys from Chlorometallate-based Ionic Liquids	222
8.5	Nanocrystalline Metals from Air- and Water-stable Ionic Liquids	227
8.6	Conclusion and Outlook	234
	Acknowledgement	235
	References	235
9	Electrodeposition on the Nanometer Scale: <i>In Situ</i> Scanning Tunneling Microscopy	239
	<i>Frank Endres, and Sherif Zein El Abedin</i>	
9.1	Introduction	239
9.2	<i>In situ</i> STM in [Py _{1,4}] TFSA	241
9.3	Electrodeposition of Aluminum	245
9.4	Electrodeposition of Tantalum	250
9.5	Electrodeposition of Poly(p-phenylene)	252
9.6	Summary	256
	References	256
10	Plasma Electrochemistry with Ionic Liquids	259
	<i>Jürgen Janek, Marcus Rohnke, Manuel Pölleth, and Sebastian A. Meiss</i>	
10.1	Introduction	259
10.2	Concepts and Principles	260
10.3	Early Studies	265
10.4	The Stability of Ionic Liquids in Plasma Experiments	269
10.5	Plasma Electrochemical Metal Deposition in Ionic Liquids	274
10.6	Conclusions and Outlook	282
	Acknowledgement	283
	References	283
11	Technical Aspects	287
	<i>Debbie S. Silvester, Emma I. Rogers, Richard G. Compton, Katy J. McKenzie, Karl S. Ryder, Frank Endres, Douglas MacFarlane, and Andrew P. Abbott</i>	
11.1	Metal Dissolution Processes/Counter Electrode Reactions	287
11.2	Reference Electrodes for Use in Room-temperature Ionic Liquids	296
11.3	Process Scale Up	310

11.4	Towards Regeneration and Reuse of Ionic Liquids in Electroplating	319
11.5	Impurities	334
	Appendix: Protocol for the Deposition of Zinc from a Type III Ionic Liquid	344
	References	345
12	Plating Protocols	353
	<i>Frank Endres, Sherif Zein El Abedin, Q. Liu, Douglas R. MacFarlane, Karl S. Ryder, and Andrew P. Abbott</i>	
12.1	Electrodeposition of Al from 1-Ethyl-3-methylimidazolium chloride/ AlCl_3	353
12.2	Electrodeposition of Al from 1-Butyl-3-methylimidazolium chloride- AlCl_3 – Toluene	356
12.3	Electrodeposition of Al from 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide/ AlCl_3	358
12.4	Electrodeposition of Al from 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide/ AlCl_3	360
12.5	Electrodeposition of Li from 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide/Lithium bis(trifluoromethylsulfonyl)amide	362
12.6	Electrodeposition of Ta from 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide	364
12.7	Electrodeposition of Zinc Coatings from a Choline Chloride: Ethylene Glycol-based Deep Eutectic Solvent	365
	References	367
13	Future Directions and Challenges	369
	<i>Frank Endres, Andrew P. Abbott, and Douglas MacFarlane</i>	
13.1	Impurities	369
13.2	Counter Electrodes/Compartments	370
13.3	Ionic Liquids for Reactive (Nano-)materials	371
13.4	Nanomaterials/Nanoparticles	372
13.5	Cation/Anion Effects	373
13.6	Polymers for Batteries and Solar Cells	373
13.7	Variable Temperature Studies	374
13.8	Intrinsic Process Safety	374
13.9	Economics (Price, Recycling)	375
13.10	Which Liquid to Start With?	375
13.11	Fundamental Knowledge Gaps	376
	Subject Index	379

Preface

Around ten years ago there were only about twenty papers per year dealing with “ionic liquids” or “room-temperature molten salts”. Hence the term “ionic liquid” was unknown to most of the scientific community at that time. Furthermore, there was practically no knowledge of it in industry, and just a handful of groups worldwide were investigating ionic liquids. Ionic liquids were perceived as an academic curiosity. When one of us (F.E.) started his independent research in 1996 with the subject “room-temperature molten salts” many people cautioned him about the eccentric topic. What was the reason for these opinions? From the 1950s to about 1995 most of the people in the community performed studies with ionic liquids based on AlCl_3 , often called “first generation” ionic liquids. These are hygroscopic liquids, liberating HCl and a variety of oxo-chloroaluminates upon exposure to moisture. Reproducible operation in these liquids requires either a strictly controlled inert gas atmosphere with extremely low water concentration or at least closed vessel conditions with limited contamination. Thus, these liquids were considered to be difficult to work with and of little practical importance. On the other hand as “room-temperature molten salts” they had attractive electrochemical windows and allowed the electrodeposition of noble metals and of aluminum and its alloys in micrometer thick layers. Aluminum is quite an interesting metal as it is self-passivating, thus under air it forms spontaneously an oxide layer which protects the metal underneath from further corrosion.

It was John Wilkes who realized that “room-temperature molten salts” would only experience a widespread interest and uptake if they were stable under environmental conditions. Wilkes’ group published details of the first such liquid in 1992 using the BF_4^- and the PF_6^- anions, the latter showing a miscibility gap with water. Thus these liquids could, in principle, be made water free. (Today we know that ionic liquids containing BF_4^- and PF_6^- are subject to decomposition in the presence of water.) Electrochemical studies showed that even these “early” ionic liquids had wide electrochemical windows of about 4 V with cathodic limits of -2 to -2.5 V. vs. NHE. This cathodic limit should, from the thermodynamic point of view, be wide enough to electrodeposit many reactive elements.

Around 1995, Seddon realized that the expression “room-temperature molten salts” was counter-productive. The expression “molten salt” was always associated with “high temperature”, as also the editors (and many authors) of this book had

to experience. The introduction of the term “ionic liquids” for low melting molten salts with melting temperatures below 100°C (the definition was actually coined by Walden in 1914) created a clear distinction and the new term “ionic liquid” began to appear in an unprecedented number of publications. In the late 1990s the first papers on the electrodeposition of silver and copper in ionic liquids based on BF_4^- and PF_6^- appeared in the literature. From these early papers it was immediately clear that electrodeposition from ionic liquids is not trivial and is actually more complicated than using ionic liquids based on AlCl_3 . In addition to viscosity and conductivity concerns, impurities such as water, halides and organic compounds proved to be major difficulties.

Thus, nearly twenty years of accumulated knowledge on AlCl_3 -based ionic liquids could only be transferred with difficulty to this new class of ionic liquids, because their Lewis acidity/basicity was totally different. Thus, the electrochemistry of these second generation ionic liquids had to be re-invented, more or less. Nevertheless, progress was not slowed and in 2002 alone there were already 600 papers dealing with ionic liquids, about 10% concentrating on electrochemical aspects. In the following years more stable ionic liquids with wider electrochemical windows were developed and cathodic decomposition potentials as low as -3 V vs. NHE were reported, opening the door to the electrodeposition of many reactive elements such as Si, Ge, Ta, Al.

Recently a novel class of deep eutectic solvents based on choline chloride have been developed. These can be handled easily under environmental conditions and circumvent many problems that occur in aqueous solutions. They also offer the first economically viable liquids that can be used on an industrial scale. As the interest of electrochemists and classical electroplaters in ionic liquids has risen strongly in the last few years we decided, in 2006, to collect the key aspects of the electrodeposition from ionic liquids in the present book. The book has been written by a panel of expert authors during late 2006 and the first half of 2007 and thus describes the state of the art as of that point in time.

In Chapter 1 we explain the motivation and basic concepts of electrodeposition from ionic liquids. In Chapter 2 an introduction to the principles of ionic liquids synthesis is provided as background for those who may be using these materials for the first time. While most of the ionic liquids discussed in this book are available from commercial sources it is important that the reader is aware of the synthetic methods so that impurity issues are clearly understood. Nonetheless, since a comprehensive summary is beyond the scope of this book the reader is referred for more details to the second edition of *Ionic Liquids in Synthesis*, edited by Peter Wasserscheid and Tom Welton. Chapter 3 summarizes the physical properties of ionic liquids, and in Chapter 4 selected electrodeposition results are presented. Chapter 4 also highlights some of the troublesome aspects of ionic liquid use. One might expect that with a decomposition potential down to -3 V vs. NHE all available elements could be deposited; unfortunately, the situation is not as simple as that and the deposition of tantalum is discussed as an example of the issues. In Chapters 5 to 7 the electrodeposition of alloys is reviewed, together with the deposition of semiconductors and conducting polymers. The deposition of conducting polymers

is still a little neglected in the literature, although the wide anodic decomposition limit allows even benzene to be easily polymerized to poly(*p*-phenylene) in ionic liquids.

Chapter 8 summarizes the principles of nanometal deposition as well as the few examples of nanometal deposition in ionic liquids. Chapter 9 shows how scanning probe microscopy can be used to study the electrodeposition of metals on the submicro- and nano-scale. *In situ* STM is also used to probe impurities in the ultralow concentration regime. Chapter 10 is devoted to a novel field in the scene, i.e. plasma electrochemistry. By applying a glow-discharge plasma to the surface of an ionic liquid which contains metal ions, suspensions of nanoparticles can be made that might be of interest, for example, as catalysts. Chapter 11 is devoted to technical aspects such as counter electrode reactions, reference electrodes (a very complicated subject), upscaling, recycling and impurities. As industry increases the scale of production the focus on cost and purity will be of increasing importance. In Chapter 12 we provide some plating protocols, which will enable the reader to begin electrodeposition experiments in ionic liquids. In Chapter 13 we have tried to summarize the future directions of the field as we see them and challenging aspects which, in our opinion, warrant further study. Of course, as the field is in a permanent state of development, such a chapter can hardly be comprehensive, but we hope that our thoughts, which are based on many years of experience, will help to stimulate further the field of “electrodeposition from ionic liquids”.

Frank Endres, Andrew Abbott and Douglas R. MacFarlane
Yokohama, Japan, December 2007

Foreword

It is always an honour to be asked to write a foreword for what is clearly an important book, but it is also a curse! What can you say that is original and interesting? – Particularly when the editors themselves have written a Preface!! But this IS an important book – electrodeposition is at the roots and heart of ionic liquid technology. It was one of the earliest applications of ionic liquids, and currently is one of the exciting areas which are developing at an amazing rate. It is a wonderful example of industrial processes developing hand-in-hand with academic research. So, I accepted this cursed honour, and am very glad that I did: the opportunity to see the chapters of this book in advance has been a privilege.

So let's start with the obvious. This book on electrodeposition from ionic liquids comes on the tail of another excellent Wiley book, edited in 2005 by Hiroyuki Ohno, entitled "Electrochemical Aspects of Ionic Liquids", an updated revision of a 2003 Japanese volume with the title "Ionic Liquids: The Front and Future of Material Development" (CMC Press, Tokyo). Is there any overlap? Well, in the thirty-two chapters of this earlier edited book, which covers the whole spectrum of electrochemistry in ionic liquids, there were only twenty pages devoted to the topic of electrodeposition (an article by Yasushi Katayama). So, there is no significant overlap to worry about.

Then, there is the whole question of the philosophy of the edited book? Has it holistic value, or is it just a random collection of articles by disparate authors? Well, the editors here have taken the same approach as Wasserscheid and Welton ("Ionic Liquids in Synthesis", 2nd Edit., Wiley-VCH, 2007). There is a well developed plan for the book, and the chapters are integrated, and dovetail well. In addition, the authors have been carefully selected – this is a book written by the leading lights of the field. The editors have done an excellent job of producing a volume which deals with the literature, conceptual framework, and practical aspects of the subject. It was particularly pleasing to see chapters and sections dealing with the problems associated with the area, including impurities, recycling and scale-up, reference electrodes, and counter electrodes. Further, as one might expect with Andy Abbott as one of the editors, there is a clear distinction drawn between ionic liquids and deep eutectic solvents.

So, is this book perfect? Well, no! One thing drove me to distraction, and it is a problem redolent of the wider literature – the choice of abbreviations

for the ionic liquids – or, more precisely, the lack of choice! Different chapters used different systems, and each cation and anion was represented in at least four ways within the book (meaning up to, or more than, sixteen possible abbreviations for some ionic liquids. For the simple, symmetrical and common ionic liquid cation, 1,3-dimethylimidazolium, there were five different abbreviations used: [MMIM], [mmim], [C₁mim], [C₁MIM], and [DMIM]; for 1-butyl-1-methylpyrrolidinium, there were six different abbreviations used: [Py_{1,4}], P_{1,4}, [BMP], BuMePy, [c₄mpyr], and [c₄mpyrr]. And, even more bizarrely, for the common anion bis(trifluoromethylsulfonyl)amide, six different abbreviations were used: (CF₃SO₂)₂N, NTF, Tf₂N, NTF₂, TFSI, and TFSA. Thus, in principle (I didn't count!), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide could have had thirty-six possible abbreviations!! This is way past ridiculous. But the problem doesn't just lie with the editors; this is reflection of the problem in the wider literature. The burgeoning of the ionic liquid literature during the past decade has meant that there has been no period of stability during which a consensus could be reached. The question of a uniform system, and the wider question of the fundamental definition of an ionic liquid, will have to be addressed elsewhere – the problem is manifest here, however. Another minor issue is that some of the English has a distinctly Germanic ring to it – but never to the point of obscuring the meaning.

To summarise then, this book is timely and edited by three of the four main experts in the field. It is planned with meticulous detail, and – of paramount importance – it is authoritative. It is inconceivable that any researcher in the future will not need access to this book, and it will be extensively cited. I congratulate Frank, Doug and Andy on a wonderful volume. Editing books of this type is a service to the community (no one does it for the royalties!), and we owe them a debt of gratitude for the huge investment of time they have made.

Kenneth R. Seddon
The QUILL Research Centre
The Queen's University of Belfast
Belfast, B9 5AG, U.K.

List of Contributors

Andrew P. Abbott

Chemistry Department
University of Leicester
Leicester LE1 7RH
UK

Tom Beyersdorff

IOLITEG GmbH & Co. KG
Ferdinand-Porsche-Straße 5/1
79211 Denzlinger
Germany

Natalia Borisenko

Faculty of Natural and Materials
Sciences
Clausthal University of Technology
38678 Clausthal-Zellerfeld
Germany

Po-Yu Chen

Faculty of Medicinal and Applied
Chemistry
Kaohsiung Medical University
807 Kaohsiung
Taiwan

Richard G. Compton

Oxford University
Physical and Theoretical Chemistry
Laboratory
South Parks Road
Oxford OX1 3QZ
United Kingdom

Jan Dalrymple

C-Tech Innovation Ltd.
C-Tech
United Kingdom

Frank Endres

Faculty of Natural and Materials
Sciences
Clausthal University of Technology
38678 Clausthal-Zellerfeld
Germany
Email: frank.endres@tu-clausthal.de

Maria Forsyth

Australian Centre of Excellence for
Electromaterials Science
Department of Materials Engineering
Monash University
Wellington Road
Clayton
VIC 3800
Australia

Rolf Hempelmann

Physical Chemistry Department
Saarland University
66123 Saarbrücken
Germany

Jürgen Janek

Physikalisch-Chemisches Institut
Justus-Liebig-Universität Giessen
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Qunxian Liu

Faculty of Natural and Material
Sciences
Clausthal University of Technology
38678 Clausthal-Zellerfeld
Germany

Douglas MacFarlane

School of Chemistry
Monash University
Wellington Road
Clayton
VIC 3800
Australia

Katy J. McKenzie

Chemistry Department
University of Leicester
Leicester LE1 7RH
UK

Sebastian A. Meiss

Physikalisch-Chemisches Institut
Justus-Liebig-Universitaet Giessen
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Harald Natter

Physical Chemistry Department
Saarland University
66123 Saarbrücken
Germany
Email: h.natter@mx.uni-saarland.de

Hiroyuki Ohno

Department of Biotechnology
Tokyo University of Agriculture and
Technology
2-24-16 Nakacho, Koganei
Tokyo 184-8588
Japan

Will Pitner

Merck KGaA
PLS R&D LSS Ionic Liquids 1
Frankfurter Str. 250
64271 Darmstadt
Germany

Manuel Pölleth

Physikalisch-Chemisches Institut
Justus-Liebig-Universitaet Giessen
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Jennifer M. Pringle

School of Chemistry
Monash University
Wellington Road
Clayton
VIC 3800
Australia
Email: Jenny.Pringle@sci.monash.edu.
au

Emma I. Rogers

Oxford University
Physical and Theoretical Chemistry
Laboratory
South Parks Road
Oxford OX1 3QZ
United Kingdom

Marcus Rohnke

Physikalisch-Chemisches Institut
Justus-Liebig-Universitaet Giessen
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Karl S. Ryder

Chemistry Department
University of Leicester
Leicester LE1 7RH
UK

Thomas J. S. Schubert

Managing Director
IOLITEC GmbH & Co. KG
Ferdinand-Porsche-Straße 5/1
79211 Denzlingen
Germany

Debbie S. Silvester

Oxford University
Physical and Theoretical Chemistry
Laboratory
South Parks Road
Oxford OX1 3QZ
United Kingdom

I.-Wen Sun

Department of Chemistry
National Cheng Kung University
Tainan 70101
Taiwan

Jorg Thöming

UFT
Section of Chemical Engineering –
Regeneration and Recycling
University of Bremen,
Leobener Str.
28359 Bremen
Germany

Daniel Waterkamp

UFT
Section of Chemical Engineering –
Regeneration and Recycling
University of Bremen,
Leobener Str.
28359 Bremen
Germany

Urs Welz-Biermann

New Business- Chemicals/Ionic
Liquids (NB-C)
Merck KGaA
NB-C, D1/311
Frankfurter Str. 250
64293 Darmstadt
Germany

Sherif Zein El Abedin

Faculty of Natural and Materials
Sciences
Clausthal University of Technology
38678 Clausthal-Zellerfeld
Germany
Permanent address:
Electrochemistry and Corrosion
Laboratory
National Research Centre
Dokki
Cairo
Egypt

List of Abbreviations

Cations:

Pyrrolidinium cations:

1-Butyl-1-methylpyrrolidinium:	[Py _{1,4}], P _{1,4} , [BMP], BuMePy, [c ₄ mpyr], [c ₄ mpyrr]
1-Propyl-1-methylpyrrolidinium:	P _{1,3}

Imidazolium Cations

1-Methyl-3-methylimidazolium:	[MMIM], [mmim], [C ₁ mim], [C ₁ MIM], [DMIM]
1-Ethyl-3-methylimidazolium:	[EMIM], [emim], [C ₂ mim], [C ₂ MIM]
1-Propyl-3-methylimidazolium:	[PMIM], [pmim], [C ₃ mim], [C ₃ MIM]
1-Butyl-3-methylimidazolium:	[BMIM], [bmim], [C ₄ mim]
1-Butyl-3-butylimidazolium:	[BBIM], [bbim]
1-Butyl-3H-imidazolium:	[Hbim]
1-Ethyl-3H-imidazolium:	[Heim]
1-Hexyl-3-methylimidazolium:	[HMIM], [hmim], [C ₆ mim], [HMPL]
1-Octyl-3-methylimidazolium:	[OMIM], [omim], [C ₈ mim]
1-Propyl-2,3-dimethylimidazolium:	[p-DiMIM], [DMPIM]
1-Butyl-2,3-dimethylimidazolium:	[b-DiMIM], [C ₄ -DMIM]
1-Etyl-2,3-dimethylimidazolium:	[e-DiMIM]
1-Hexyl-2,3-dimethylimidazolium:	[C ₆ -DMIM]
1-Decyl-3-methylimidazolium:	[decyl-MIM], [C ₁₀ MIM], [C ₁₀ mim]
1-Benzyl-3-methylimidazolium:	[BZMIM]
1-Hydroxyethyl-3-methylimidazolium:	[HO(CH ₂) ₂ MIM], [C ₂ OHMIM]
1,2-Di-ethyl-3,4-dimethylimidazolium:	[DEDMIM]
1-Alkyl-3-methylimidazolium:	[C _n MIM], [C _n mim]
1-(2-hydroxyethyl)-3-methylimidazolium:	[C ₂ OHmim]
1-(2-methoxyethyl)-3-methylimidazolium:	[C ₃ Omim]
1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium:	[C ₅ O ₂ mim]

Pyridinium Cations:

N-Methylpyridinium	[MP]
N-Ethylpyridinium	[EP], [C ₂ py], [EtPy]
N-Propylpyridinium	[PP]
N-Butylpyridinium:	[BP], [bpyr], [bpyrr], [C ₄ py]
N-Hexylpyridinium:	[HP], [HPYR], [C ₁₆ py]

Piperidinium Cations:

N-Ethyl-N-methylpiperidinium:	[C ₂ mPip]
N-Propyl-N-methylpiperidinium:	[C ₃ mPip], [PP ₁₃]
N-Butyl-N-methylpiperidinium:	[C ₄ mPip], [PP ₁₄]

Phosphonium Cations:

Tri-hexyl-tetradecylphosphonium:	[Ph ₃ t], [P _{14,6,6,6}], [P _{6,6,6,14}]
----------------------------------	---

Pyrazolium Cations:

N,N-Diethyl-3-methylpyrazolium	[DEMPZ]
--------------------------------	---------

Ammonium-Cations:

Trimethylammonium:	[TMHA]
Tetramethylammonium:	[N ₁₁₁₁], [TMA]
1,1,1-Trimethyl-1-methoxyethylammonium:	[N _{111,2O1}]
Butyl-trimethylammonium:	[N ₁₁₁₄], [N ₄₁₁₁], [BTMA]
Benzyl-trimethylammonium:	[BTMA]
Propyl-trimethylammonium:	[N ₁₁₁₃], [N ₃₁₁₁], [PTMA]
1-Cyanomethyl-1,1,1-trimethylammonium:	[N _{111,1-CN}]
1,1-Dimethyl-1-ethyl-1-methoxyethylammonium:	[N _{112,2O1}]
1,1-Diethyl-1-methyl-1-methoxyethylammonium:	[N _{122,2O1}]
Tributyl-methylammonium:	[N ₄₄₄₁], [TBMA]
Trimethyl-n-hexylammonium:	[N ₁₁₁₆], [TMHA]
Tetraethylammonium:	[N ₂₂₂₂], [TEA]
Triethyl-hexylammonium:	[N ₂₂₂₆]
Tetrabutylammonium:	[N ₄₄₄₄], [TBA], Bu ₄ N
Triethyl-hexylammonium:	[N ₆₂₂₂]
Hydroxyethyl-trimethylammonium:	[Me ₃ NC ₂ H ₄ OH], Ch also called choline
Butyl-diethyl-methylammonium:	[N ₁₂₂₄]

Sulfonium Cations:

Trimethylsulfonium:	[S ₁₁₁]
Triethylsulfonium:	TES, [S ₂₂₂]
Tributylsulfonium:	TBS, [S ₄₄₄]

Anions:

Bis(trifluoromethylsulfonyl) amide:	(CF ₃ SO ₂) ₂ N, NTF, Tf ₂ N, NTf ₂ , TFSI, TFSA Sometimes this anion is also called bis(trifluoromethylsulfonyl)imide or bistriflamide, bistriflimide
Trispentafluoroethyl-trifluorophosphate:	FAP
Trifluoroacetate:	ATF, TFA
Trifluoromethylsulfonate:	OTF, OTf, TFO, Tf Also called trifluoromethanesulfonate
Dicyanoamide:	DCA
Tricyanomethide:	TCM
Tetracyanoborate:	TCB
Tetraphenylborate:	[BPh ₄]
Tris(trifluoromethylsulfonyl) methide:	[CTf ₃]
Thiocyanate:	SCN

Other chemicals:

[CHES]:	2-(Cyclohexylamino)ethylsulfonate
ChCl:	Choline chloride
DCM:	Dichloromethane
EDOT:	Ethylenedioxythiophene
EG:	Ethyleneglycole
Fc:	Ferrocene
Fc ⁺ :	Ferrocinium
GC:	Glassy carbon
ITO:	Indium-tin-oxide
PC:	Propylenecarbonate
PEDOT:	Polyethylenedioxythiophene
TMPD:	Tetramethylphenylenediamine
TMS:	Tetramethylsilane

Abbreviations:

AAS:	Atomic Absorption Spectroscopy
ACD:	Anomalous Codeposition
AFM:	Atomic Force Microscopy
ATR-FTIR:	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

BASIL:	Biphasic Acid Scavenging Utilizing Ionic Liquids
CIS:	Copper-indium-selenide
CV:	Cyclic Voltammetry
CVD:	Chemical Vapor Deposition
DSSC:	Dye Sensitized Solar Cell
ECAL:	Electrochemical Atomic Layer Epitaxy
EC-STM:	Electrochemical in situ scanning tunnelling microscopy
EDX, EDS, EDAX:	Energy Dispersive X-ray analysis
EIS:	Electrochemical Impedance Spectroscopy
EMF:	Electromotive Force
EQCM:	Electrochemical Quartz Crystal Microbalance
FAB MS:	Fast atom bombardment mass spectroscopy
FFG-NMR:	Fixed Field Gradient Nuclear Magnetic Resonance Spectroscopy
FWHM:	Full width at half maximum
HBD:	Hydrogen Bond Donor
HOPG:	Highly Oriented Pyrolytic Graphite
HO-ESY:	Heteronuclear Overhauser Effect Spectroscopy
H-REM, H-SEM:	High Resolution Scanning Electron Microscopy
H-TEM:	High Resolution Transmission Electron Microscopy
ICP:	Inductively Coupled Plasma (Spectroscopy)
LCA:	Life Cycle Analysis
LED:	Light Emitting Diode
LSV:	Linear Sweep Voltammetry
MBE:	Molecular Beam Epitaxy
MNDO:	Modified neglect of diatomic overlap
NHE:	Normal Hydrogen Electrode
NMR:	Nuclear Magnetic Resonance
OCP:	Open Circuit Potential
OPD:	Overpotential deposition
PECD:	Plasmaelectrochemical deposition
PED:	Pulsed Electrodeposition
PLED:	Polymer Light Emitting Diode
PPP:	Poly-para-phenylene
PVD:	Physical Vapour Deposition
RTIL:	Room Temperature Ionic Liquid
SAED:	Selected Area Electron Diffraction
SIGAL:	Siemens Galvano-Aluminium
STM:	Scanning Tunnelling Microscopy
TSIL:	Task Specific Ionic Liquid
UPD:	Underpotential deposition
UHV:	Ultrahigh Vacuum
VFT, VTF:	Vogel-Tammann-Fulcher
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction

1

Why use Ionic Liquids for Electrodeposition?

Andrew P. Abbott, Ian Dalrymple, Frank Endres, and Douglas R. MacFarlane

With any great voyage of discovery the explorer should always be asked at the outset “Why are you doing this?” To answer the question “Why use ionic liquids for electrodeposition?” it is first necessary to look at current best practice and find its limitations.

It is widely recognised that in 1805 Italian chemist, Luigi Brugnatelli made the first experiments in what we now know as electroplating. Brugnatelli used the newly discovered Voltaic Pile to deposit gold “I have lately gilt in a complete manner two large silver medals, by bringing them into communication by means of a steel wire, with a negative pole of a voltaic pile, and keeping them one after the other immersed in ammoniuret of gold newly made and well saturated” [1]. The process was later improved by John Wright who found that potassium cyanide was a beneficial electrolyte to add for silver and gold plating as it allowed thick adherent deposits to be obtained. Until the middle of the 19th century the production of jewellery and the gilding of decorative items were the main uses of electrodeposition.

With an increased understanding of electrochemistry, the practice of metal deposition spread to non-decorative metals such as nickel, brass, tin, and zinc by the 1850s. Even though electroplated goods entered many aspects of manufacturing industry very little changed about the physical processes involved in electrodeposition for about 100 years. It was only with the advent of the electronics industry in the middle of the 20th century that significant changes occurred in the hardware and chemistry of the plating solutions. The post-war period saw an increase in gold plating for electronic components and the use of less hazardous plating solutions. This trend has continued with increased control of hazardous materials to the environment. Improved solution composition and power supply technology has allowed the development of fast and continuous plating of wire, metal strips, semiconductors and complex substrate geometries.

Many of the technological developments seen in the electronics industry depend upon sophisticated electroplating including the use of exotic metals and this is one of the drivers for new technology within the electroplating sector. The other

main driver is the search for alternative technologies for metals such as chromium, nickel and cadmium. Anti-corrosion and wear-resistant coatings are predominant markets in the electroplating sector and environmental directives will evidently limit their usage in the future.

The main metals of that commercially deposited are Cr, Ni, Cu, Au, Ag, Zn and Cd together with a number of copper and zinc-based alloys [1]. The whole electroplating sector is based on aqueous solutions. There are some niche markets based on organic solvents such as aluminum but these are very much exceptions. Metals outside this list are generally deposited using plasma or chemical vapor deposition techniques (PVD and CVD). These methods allow the coating of most substrates (metal, plastic, glass, ceramic etc.) not only with metal but also with alloys or compounds (oxide, nitride, carbide, etc.), without damaging the environment. Although these techniques are technically interesting, it is regrettable that they always involve high capital investment and it is difficult to prepare thick coatings, thus they are only applied to high value niche markets.

Clearly the key advantages of using aqueous solutions are:

- Cost
- Non-flammable
- High solubility of electrolytes
- High conductivities resulting in low ohmic losses and good throwing power
- High solubility of metal salts
- High rates of mass transfer.

For these reasons water will remain the mainstay of the metal plating industry, however, there are also limitations of aqueous solutions including:

- Limited potential windows
- Gas evolution processes can be technically difficult to handle and result in hydrogen embrittlement
- Passivation of metals can cause difficulties with both anodic and cathodic materials
- Necessity for complexing agents such as cyanide
- All water must eventually be returned to the water course.

These prevent aqueous solutions being applied to the deposition of several technically important materials.

The key technological goals include replacement of environmentally toxic metal coatings, deposition of new alloys and semiconductors and new coating methods for reactive metals. The main driving force for non-aqueous electrolytes has been the desire to deposit refractory metals such as Ti, Al and W. These metals are abundant and excellent for corrosion resistance. It is, however, the stability of their oxides that makes these metals difficult to extract from minerals and apply as surface coatings.

1.1

Non-aqueous Solutions

There is clearly a range of alternative non-aqueous solutions that could be used. Ideally, to obtain the properties required for an electrolyte solution, polar molecules have to be used and these should preferably be small to obtain the requisite high fluidity. Unfortunately, all polar molecules result from having electronegative elements which by their nature makes them good electron donors. Accordingly, they will strongly coordinate to metal ions making them difficult to reduce. While a number of metals have been deposited from polar organic solvents these tend to be the rather noble metals and the processes offer few advantages over aqueous solutions. Some studies have been made using non-polar organic solvents, predominantly aromatic hydrocarbons but these suffer from the serious disadvantage that the dissolved electrolytes are highly associated and the solutions suffer from poor conductivity. The solutions do, however, have wide potential windows and it has been demonstrated that metals such as aluminum and titanium (Ti at least in very thin layers) can be deposited from them. One of the most successful non-aqueous processes is the SIGAL process developed in the late 1980s for the deposition of aluminum from toluene [2, 3]. The aluminum source is triethyl aluminum which is pyrophoric and, despite the high flammability of the electrolyte solution, the process has been commercialized and is currently the only electrochemical method for the deposition of aluminum. A review of electrochemistry in non-aqueous solutions is given by Izutsu [4].

1.2

Ionic Fluids

Clearly an alternative to molecular solvents is the use of ionic fluids. Ionic materials usually melt at high temperatures due to their large lattice energies. High-temperature molten salts have been extensively used for the electrowinning of metals such as Li, Na, Ti and Al at temperatures of up to 1000 °C [5–7]. They have wide potential windows, high conductivities and high solubilities for metal salts, in fact they have most of the advantages of aqueous solutions and overcome most of the limitations of aqueous solutions, but clearly they suffer from the major limitation that the operational conditions are difficult to achieve and limit the range of substrates that can be used for deposition.

The alternative to high-temperature molten salts is to use an ionic substance that melts at a low temperature. While this may sound like an oxymoron it is logical to suppose that the melting point of an ionic substance is related to ionic size and if the ions are made large enough the material will eventually melt at ambient conditions. A significant amount of work was carried out in the middle of the 20th century with the aim of developing lower temperature molten salts. One of the key aims was a lower temperature melt for aluminum deposition which led

to the formation of $\text{Li}^+ / \text{K}^+ / \text{AlCl}_3$ eutectics which have freezing points close to 100°C [8]. These low freezing points arise due to the large chloroaluminate anions (AlCl_4^- and Al_2Cl_7^-) that form in the eutectic mixtures and have low lattice energies. The use of quaternary ammonium salts, particularly pyridinium and imidazolium salts, has pushed the freezing point down to ambient conditions. The term “ionic liquids” was coined to distinguish these lower temperature ionic fluids from the high temperature analogues which are composed predominantly of inorganic ions.

The synthesis and properties of a range of ionic liquids are briefly summarized in the following chapter while the history and chemical properties of these liquids are covered in several well known reviews [9–12]. Several applications of ionic liquids are being tested and these are as diverse as fuel desulfurization [13] and precious metal processing [14] but few have yet come to practical fruition.

BASF's BASIL process [15] and the Dimersol[®] process [16] have both been commercialized. The former uses the ionic liquid as a phase transfer catalyst to produce alkoxyphenylphosphines which are precursors for the synthesis of photoinitiators used in printing inks and wood coatings. The imidazole acts as a proton scavenger in the reaction of phenyl-chlorophosphines with alcohols to produce phosphines. The Dimersol[®] process uses a Lewis acid catalyst for the dimerization of butenes to produce C_8 olefins which are usually further hydroformylated giving C_9 alcohols used in the manufacture of plasticizers. Several other processes are also at the pilot plant scale and some ionic liquids are used commercially as additive e.g. binders in paints.

1.3

What is an Ionic Liquid?

The recognised definition of an ionic liquid is “an ionic material that is liquid below 100°C ” but leaves the significant question as to what constitutes an ionic material. Some authors limit the definition to cations with discrete anions e.g. BF_4^- , NO_3^- . This definition excludes the original work on chloroaluminate systems and the considerable work on other eutectic systems and is therefore unsatisfactory. Systems with anionic species formed by complex equilibria are difficult to categorise as the relative amounts of ionic species depend strongly on the composition of the different components.

Ionic liquids have also been separated into first and second generation liquids [10]; where first generation liquids are those based on eutectics and second generation have discrete anions [17]. Others have sought to further divide the first generation liquids into separate types depending on the nature of the Lewis or Brønsted acid that complexes [18]. While there is some dispute whether eutectics with Brønsted acids constitute ionic liquids at all there are others who seek to widen the description of ionic liquids to include materials such as salt hydrates [19].

In general, ionic liquids form because the charge on the ions is delocalized and this gives rise to a reduction in lattice energy. The majority of ionic liquids are

described by the equilibrium:



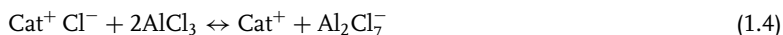
Potentially, complex cations could also be formed using species such as cryptands or crown ethers:



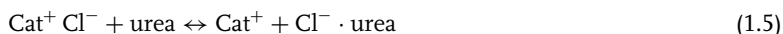
The confusion arises from the magnitude of the equilibrium constant. For discrete anions such as BF_4^- and even $((\text{CF}_3\text{SO}_2)_2\text{N})^-$ the equilibrium lies clearly to the right of Eq. (1.1). For some eutectic-based liquids the equilibrium constant is also to the right e.g.



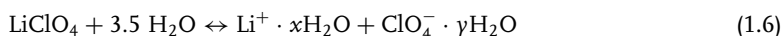
But the addition of more Lewis acid produces other anionic species.



The use of less Lewis acidic metals e.g. ZnCl_2 or SnCl_2 will lead to a small amount of Cl^- . The species formed between the anion and the complexing agent becomes weaker when a Brønsted acid e.g. urea is used [18].



Others have claimed that, in the extreme, water can act as a good Brønsted acid and, in the extreme, hydrate salts can act as ionic liquids [19].



Ionic liquids with discrete anions have a fixed anion structure but in the eutectic-based liquids at some composition point the Lewis or Brønsted acid will be in considerable excess and the system becomes a solution of salt in the acid. A similar scenario also exists with the incorporation of diluents or impurities and hence we need to define at what composition an ionic liquid is formed. Many ionic liquids with discrete anions are hydrophilic and the absorption of water is found sometimes to have a significant effect upon the viscosity and conductivity of the liquid [20–22]. Two recent approaches to overcome this difficulty have been to classify ionic liquids in terms of their charge mobility characteristics [23] and the correlation between the molar conductivity and fluidity of the liquids [24]. This latter approach is thought by some to be due to the validity of the Walden rule

$$\Lambda \eta = \text{constant} \quad (1.7)$$

in ionic liquids, where Λ is the molar conductivity and η is the viscosity. This is, however a misrepresentation of Eq. (1.7) which was found empirically and is only strictly valid for a specific ion at infinite dilution and constant temperature. The Walden rule is a useful tool for approximate classification of ionic liquids but it actually follows from the Nernst–Stokes–Einstein equation (See Chapters 2.3 and 11.3) [23]. Most importantly, deviations from the Walden rule do not necessarily show that a salt is not an ionic liquid but more usually occur where ionic species deviate from the model of centro-symmetric spherical ions with similar ionic radii. The Walden rule can, however, be used to give evidence of different charge transfer mechanisms e.g. a Grotthuss mechanism for protonic ionic liquids [24].

In this book a broad-church of ionic liquids will be assumed, encompassing all of the above types because, in the discipline of electrodeposition, it is the resultant deposit that is important rather than the means. As will be seen later there is also a very fine line between a concentrated electrolyte solution and an ionic liquid containing diluents.

1.4 Technological Potential of Ionic Liquids

A series of transition- and main group-metal-containing ionic liquids have been formulated and the feasibility of achieving electrodeposition has been demonstrated for the majority of these metals, Figure 1.1 shows the elements in the periodic table that have been deposited using ionic liquids. Details of these systems are given in the subsequent chapters and concise summaries exists in recently published reviews [18,25,26].

It must be stressed that while the deposition of a wide range of metals has been demonstrated from a number of ionic liquids the practical aspects of controlling deposit morphology have not been significantly addressed due to the complex nature of the process parameters that still need to be understood. Despite the lack of reliable models to describe mass transport and material growth in ionic liquids, there are tantalizing advantages that ionic liquid solvents have over aqueous baths that make the understanding of their properties vitally important. Some of these advantages include:

- Electroplating of a range of metals impossible to deposit in water due to hydrolysis e.g. Al, Ti, Ta, Nb, Mo, W. As an example, the deposition of Al by electrolysis in a low-temperature process has long been a highly desirable goal, with many potential applications in aerospace for anti-friction properties, as well as replacing Cr in decorative coatings. The deposition of Ti, Ta, Nb, Mo, W will open important opportunities in various industries, because of their specific properties (heat, corrosion, abrasion resistance, low or high density etc.).
- Direct electroplating of metals on water-sensitive substrate materials such as Al, Mg and light alloys with good adherence should be possible using ionic liquids.
- There is potential for quality coatings to be obtained with ionic liquids rather than with water. Currently available metallic coatings suffer from hydrogen