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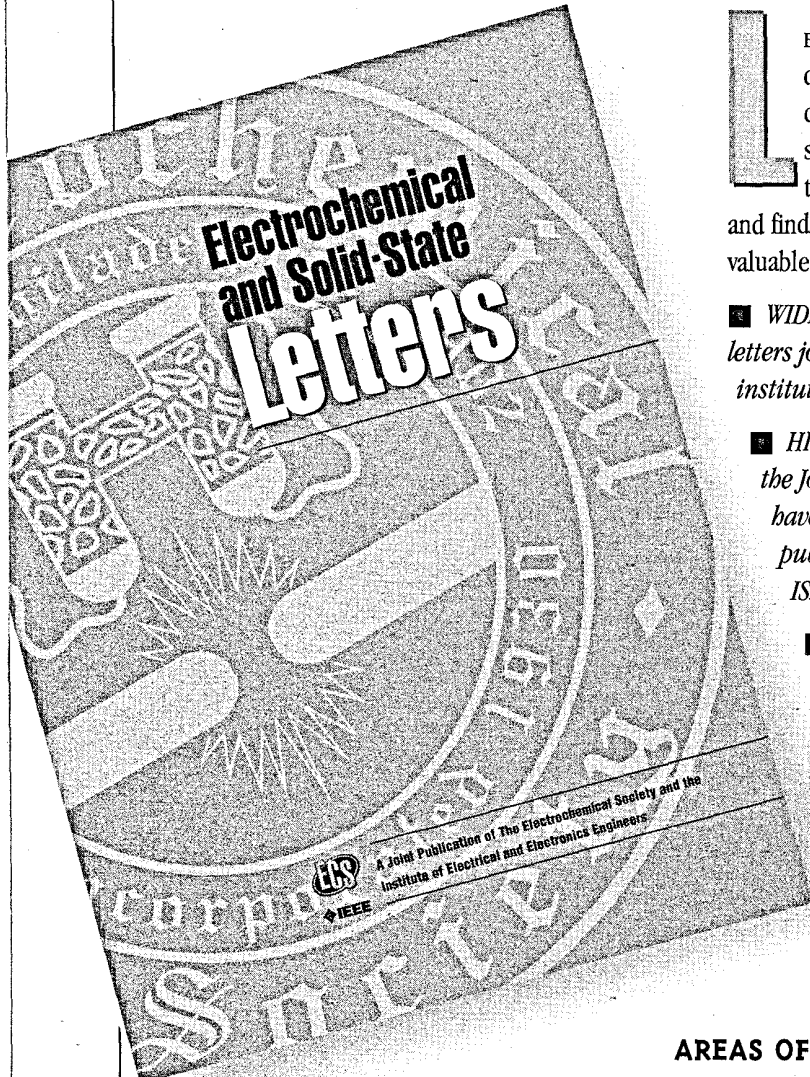


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Table of Contents

Batteries and Energy Storage

Liquid Metal Alloys as Self-Healing Negative Electrodes for Lithium Ion Batteries <i>R. D. Deshpande, J. Li, Y.-T. Cheng, M. W. Verbrugge</i>	A845
Study of Thermal-Runaway in Batteries I. Theoretical Study and Formulation <i>F. Torabi, V. Esfahanian</i>	A850
Analysis of the Lithium-Ion Insertion Silicon Composite Electrode/Separator/Lithium Foil Cell <i>R. Chandrasekaran, T. F. Fuller</i>	A859
Electrolyte Systems for High Withstand Voltage and Durability I. Linear Sulfones for Electric Double-Layer Capacitors <i>K. Chiba, T. Ueda, Y. Yamaguchi, Y. Oki, F. Shimodate, K. Naoi</i>	A872
Electrochemical Behavior of Layered Solid Solution $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M} = \text{Ni, Mn, Co}$) Li-Ion Cathodes with and without Alumina Coatings <i>W. C. West, J. Soler, M. C. Smart, B. V. Ratnakumar, S. Firdosy, V. Ravi, M. S. Anderson, J. Hrbacek, E. S. Lee, A. Manthiram</i>	A883
Evolution of Phase Transformation Behavior in $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ Cathodes Studied by In Situ XRD <i>K. Rhodes, R. Meisner, Y. Kim, N. Dudney, C. Daniel</i>	A890
Study of the Conversion Reaction Mechanism for Copper Borate as Electrode Material in Lithium-Ion Batteries <i>G. Parzych, D. Mikhailova, S. Oswald, J. Eckert, H. Ehbrenberg</i>	A898
Thermal Treatment Effects on Manganese Dioxide Structure, Morphology and Electrochemical Performance <i>W. M. Dose, S. W. Donne</i>	A905
On the Thermal Behavior of Lithium Intercalated Graphites <i>O. Haik, S. Ganin, G. Gershinsky, E. Zinigrad, B. Markovsky, D. Aurbach, I. Halalay</i>	A913
Improved Electrochemical Performance in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Promoted by Niobium-Incorporation <i>L.-L. Zhang, X. Zhang, Y.-M. Sun, W. Luo, X.-L. Hu, X.-J. Wu, Y.-H. Huang</i>	A924
Graphene-Based Hybrid Electrode Material for High-Power Lithium-Ion Batteries <i>H. Kim, S.-W. Kim, J. Hong, H.-D. Lim, H. S. Kim, J.-K. Yoo, K. Kang</i>	A930
Study of $\text{Li}_{1+x}(\text{Mn}_{4/9}\text{Co}_{1/9}\text{Ni}_{4/9})_{1-x}\text{O}_2$ Cathode Materials for Vehicle Battery Applications <i>S.-H. Kang, W. Lu, K. G. Gallagher, S.-H. Park, V. G. Pol</i>	A936
Electrophoretic Fabrication and Characterizations of Manganese Oxide/Carbon Nanotube Nanocomposite Pseudocapacitors <i>C. J. Hung, J. H. Hung, P. Lin, T. Y. Tseng</i>	A942
Location- and Orientation-Dependent Progressive Crack Propagation in Cylindrical Graphite Electrode Particles <i>R. Grantab, V. B. Shenoy</i>	A948
Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales <i>G.-H. Kim, K. Smith, K.-J. Lee, S. Santhanagopalan, A. Pesaran</i>	A955
Facile Synthesis of Highly Conductive $\text{RuO}_2\text{-Mn}_3\text{O}_4$ Composite Nanofibers via Electrospinning and Their Electrochemical Properties <i>D.-Y. Youn, H. L. Tuller, T.-S. Hyun, D.-K. Choi, I.-D. Kim</i>	A970
A Comparative Study of Electrochemical Capacitive Behavior of NiFe_2O_4 Synthesized by Different Routes <i>S. Anwar, K. Sudalai Muthu, V. Ganesh, N. Lakshminarasimhan</i>	A976
Direct Mapping of Ion Diffusion Times on LiCoO_2 Surfaces with Nanometer Resolution <i>S. Guo, S. Jesse, S. Kalnaus, N. Balke, C. Daniel, S. V. Kalinin</i>	A982



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2011 · Vol. 158, No. 8

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Heterogeneous Through-Plane Porosity Distributions for Treated PEMFC GDLs I. PTFE Effect

Z. Fishman, A. Bazylak B841

Heterogeneous Through-Plane Porosity Distributions for Treated PEMFC GDLs. II. Effect of MPL Cracks

Z. Fishman, A. Bazylak B846

Conductivity Relaxation of Proton-Conducting BaCe_{0.85}Y_{0.15}O_{3-δ} Upon Oxidation and Reduction

D.-K. Lim, M.-B. Choi, K.-T. Lee, H.-S. Yoon, E. D. Wachsman, S.-J. Song B852

Proton Conductivity in Acceptor-Doped LaVO₄

M. Huse, T. Norby, R. Haugsrud B857

Thin Film Fuel Cell Based on Nanometer-Thick Membrane of Amorphous Zirconium Phosphate Electrolyte

Y. Aoki, Y. Fukunaga, H. Habazaki, T. Kunitake B866

A DMFC with Methanol-Tolerant-Carbon-Supported-Pt-Pd-Alloy Cathode

K. G. Nisbhanth, P. Sridhar, S. Pitchumani, A. K. Shukla B871

Diffusion Impedance Element Model for the Triple Phase Boundary

A. Dhandu, H. Pitsch, R. O'Hayre B877

Fabrication, Performance, and Model for Proton Conductive Solid Oxide Fuel Cell

C.-L. Tsai, V. H. Schmidt B885

A Combined Rotating Disk Electrode/X-Ray Diffraction Study of Co Dissolution from Pt_{1-x}Co_x Alloys

D. A. Stevens, S. Wang, R. J. Sanderson, G. C. K. Liu, G. D. Vernstrom, R. T. Atanasoski, M. K. Debe, J. R. Dahn B899

Dissolution of Ni from High Ni Content Pt_{1-x}Ni_x Alloys

D. A. Stevens, R. Mehrotra, R. J. Sanderson, G. D. Vernstrom, R. T. Atanasoski, M. K. Debe, J. R. Dahn B905

Extraordinary Oxygen Reduction Activity of Pt₃Ni₇

M. K. Debe, A. J. Steinbach, G. D. Vernstrom, S. M. Hendricks, M. J. Kurkowsky, R. T. Atanasoski, P. Kadera, D. A. Stevens, R. J. Sanderson, E. Marvel, J. R. Dahn B910

Oxygen Reduction Activity of Dealloyed Pt_{1-x}Ni_x Catalysts

G. C.-K. Liu, D. A. Stevens, J. C. Burns, R. J. Sanderson, G. Vernstrom, R. T. Atanasoski, M. K. Debe, J. R. Dahn B919

Cold Start of a Polymer-Electrolyte Fuel Cell I. Development of a Two-Dimensional Model

R. J. Balliet, J. Newman B927

Cold Start of a Polymer-Electrolyte Fuel Cell II. Model Verification Using Parametric Studies

R. J. Balliet, J. Newman B939

Cold Start of a Polymer-Electrolyte Fuel Cell III. Optimization of Operational and Configurational Parameters

R. J. Balliet, J. Newman B948

A Simple Model for Carbon Corrosion in PEM Fuel Cell

A. A. Kulikovskiy B957

Progress in In Situ X-Ray Tomographic Microscopy of Liquid Water in Gas Diffusion Layers of PEFC

J. Eller, T. Rosén, F. Marone, M. Stamparoni, A. Wokaun, F. N. Büchi B963

Influence of Oxygen Surface Exchanges on Oxygen Semi-Permeation through La_(1-x)Sr_xFe_(1-y)Ga_yO_{3-δ} Dense Membrane

P. M. Geffroy, A. Vivet, J. Fouletier, N. Richet, P. Del Gallo, T. Chartier B971

Electrochemical Analysis of Reformate-Fuelled Anode Supported SOFC

A. Kromp, A. Leonide, A. Weber, E. Ivers-Tiffée B980

Relationship among Microstructure, Ionomer Property and Proton Transport in Pseudo Catalyst Layers

H. Iden, K. Sato, A. Ohma, K. Shinohara B987

High Performance SOFC Cathode Prepared by Infiltration of $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ ($n = 1, 2$, and 3) in Porous YSZ

S. Choi, S. Yoo, J.-Y. Shin, G. Kim B995

Pulsed Laser Deposition of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ Nano-Composite and Its Application to Gradient-Structured Thin-film Cathode of SOFC

D.-H. Myung, J. Hwang, J. Hong, H.-W. Lee, B.-K. Kim, J.-H. Lee, J.-W. Son B1000

Modeling Low-Platinum-Loading Effects in Fuel-Cell Catalyst Layers

W. Yoon, A. Z. Weber B1007

Formic Acid Oxidation on $\text{Pt}_{100-x}\text{Pb}_x$ Thin Films Electrodeposited on Au

S.-M. Hwang, J. E. Bonevich, J. J. Kim, T. P. Moffat B1019

Oxygen Reduction Reaction Electrocatalytic Activity of Glancing Angle Deposited Platinum Nanorod Arrays

W. J. Khudbayer, N. N. Kariuki, X. Wang, D. J. Myers, A. U. Shaikh, T. Karabacak B1029

Microstructure of Platinum-Carbon Agglomerates with Hydrocarbon-Based Binder and Its Effect on the Cathode Performance of PEFC

J. Kawaji, S. Suzuki, Y. Takamori, T. Mizukami, M. Morishima B1042

Tubular Solid Oxide Electrolysis Cell for NO_x Decomposition

K. Hamamoto, T. Suzuki, Y. Fujisiro, M. Awano B1050

Corrosion, Passivation, and Anodic Films

The Electrochemical Corrosion Mechanisms of Pure Cr with NaCl Deposit in Water Vapor at 600°C

Y. Tang, L. Liu, Y. Li, F. Wang C237

Synthesis and Morphology of TiO_2 Nanotubes by Anodic Oxidation Using Surfactant Based Fluorinated Electrolyte

M. P. Neupane, I. S. Park, T. S. Bae, H. K. Yi, F. Watari, M. H. Lee C242

Effect of Inhibitors on the Critical Pitting Temperature of the High-Entropy Alloy $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.1}$

Y. L. Chou, J. W. Yeh, H. C. Shih C246

Electrochemical/Chemical Deposition and Etching

Electroless Deposition of Ru Films Via an Oxidative-Reductive Mechanism

J.-Y. Chen, Y.-C. Hsieh, L.-Y. Wang, P.-W. Wu D463

Predictive Analytical Fill Model of Interconnect Metallization Providing Optimal Additives Concentrations

J. Adolf, U. Landau D469

Local Epitaxial Growth of Ru Thin Films by Atomic Layer Deposition at Low Temperature

S. K. Kim, S. Han, G. H. Kim, J. H. Jang, J. H. Han, C. S. Hwang D477

Composition and Microstructure Control of Tin-Bismuth Alloys in the Pulse Plating Process

Y.-D. Tsai, C.-C. Hu D482

Influence of Doping on Ni Electroless Deposition at Single Crystalline Si

D. Lee, D. Kim, B. Yoo D490

Low Pressure Chemical Vapor Deposition of Aluminum-Doped Zinc Oxide for Transparent Conducting Electrodes

W.-H. Kim, W. J. Maeng, M.-K. Kim, H. Kim D495



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Electrodeposited Nanostructured α -Fe₂O₃ Photoanodes for Solar Water Splitting: Effect of Surface Co-Modification on Photoelectrochemical Performance

R. S. Schreiber, L. Ballesteros, A. Burgos, E. C. Muñoz, P. Grez, D. Leinen, F. Martín, J. R. Ramos-Barrado, E. A. Dalchiale D500

Electroless Deposition of Silver on Multiwalled Carbon Nanotubes Using Iodide Bath

S. Arai, J. Fujii D506

Fluorine Passivation of Titanium Oxide Films on ITO/Glass Grown by Liquid Phase Deposition for Electrochromism

M.-K. Lee, C.-H. Fan, H.-C. Wang, C.-Y. Chang D511

Effect of Carbon Modification of Particles on Their Incorporation Rate during Electrodeposition

D. Socol, J. Martens, S. Claessens, J. Fransaer D515

Reductive Eliminations from Amido Metal Complexes: Implications for Metal Film Deposition

M. Bouman, F. Zaera D524

Composition Control of the Eutectic Sn-Based Alloys: Sn-Ag, Sn-Cu, Sn-Ag-Cu, From Simple Plating Baths

Y.-D. Tsai, C.-C. Hu D527

Electrochemical Synthesis and Engineering

Formation of Nickel Nanowires via Electroless Deposition Under a Magnetic Field

M. Kawamori, S. Yagi, E. Matsubara E79

Facile Electrochemical Synthesis of ZnO/ZnS Heterostructure Nanorod Arrays

Z. Liu, X. Lu, S. Xie, J. Zhang, Z. Liu, Y. Tong E84

Crystalline-Phase-Dependent Photoluminescence and Photoconductivity of Roughened ZnO Nanostructure Grown by Self-Electrochemical Transformation

Y.-H. Pai, G.-R. Lin E88

Physical and Analytical Electrochemistry

Application of Electrochemical Method to Measure Diffusion Coefficient in Liquid Metal

T. Murakami, T. Koyama F147

Dielectric Science and Materials

Growth Characteristics and Film Properties of Cerium Dioxide Prepared by Plasma-Enhanced Atomic Layer Deposition

W.-H. Kim, M.-K. Kim, W. J. Maeng, J. Gatineau, V. Pallem, C. Dussarrat, A. Noori, D. Thompson, S. Chu, H. Kim G169

Nano-Roughened Teflon-Like Film Coated Polyethylene Terephthalate Substrate with Trifluoromethane Plasma Enhanced Hydrophobicity and Transparency

Y.-H. Pai, G.-R. Lin G173

Suppression of ALD-Induced Degradation of Ge MOS Interface Properties by Low Power Plasma Nitridation of GeO₂

R. Zhang, T. Iwasaki, N. Taoka, M. Takenaka, S. Takagi G178

Atomic Layer Deposition of Tantalum-Incorporated Hafnium Dioxide: Strategies to Enhance Thermal Stability

T. Wang, J. G. Ekerdt G185

Detection of the Tetragonal Phase in Atomic Layer Deposited La-Doped ZrO₂ Thin Films on Germanium

C. Wiemer, A. Lamperti, L. Lamagna, O. Salicio, A. Molle, M. Fanciulli G194

Characterization of Fluorinated-SiO₂/PMA-Treated TiO₂/(NH₄)₂S-Treated GaAs MOS Structure

M.-K. Lee, C.-F. Yen G199

Microstructural Evolution and Electrical Characteristics of Er-germanides Formed on Ge Substrate

V. Janardhanam, K. Moon, J.-S. Kim, M.-S. Yi, K.-S. Ahn,
C.-J. Choi H751

Single- and Dual-Layer Nanocrystalline Indium Tin Oxide Embedded ZrHfO High- k Films for Nonvolatile Memories – Material and Electrical Properties

C.-H. Lin, Y. Kuó H756

Silicon Nitride Film Removal During Chemical Mechanical Polishing Using Ceria-Based Dispersions

P. R. Veera Dandu, B. C. Peethala, H. P. Amanapu, S. V. Babu H763

Effect of Halogen-Based Neutral Beam on the Etching of $\text{Ge}_2\text{Sb}_2\text{Te}_5$

S.-K. Kang, M. H. Jeon, J. Y. Park, G. Y. Yeom, M. S. Jhon,
B. W. Koo, Y. W. Kim H768

Mechanisms of Oxygen Precipitation in Cz-Si Wafers Subjected to Rapid Thermal Anneals

A. Sarikov, V. Litovchenko, I. Lisouskyy, M. Voitovich, S. Zlobin,
V. Kladko, N. Slobodyan, V. Machulin, C. Claeys H772

Lanthanide Aluminates as Dielectrics for Non-Volatile Memory Applications: Material Aspects

C. Adelman, J. Swerts, O. Richard, T. Conard, M. Popovici,
J. Meersschant, V. V. Afanas'ev, L. Breuil, A. Cacciato, K. Opsomer,
B. Brijs, H. Tielens, G. Pourtois, H. Bender, M. Jurczak,
J. Van Houdt, S. Van Elshocht, J. A. Kittl H778

Degradation of 248 nm Deep UV Photoresist by Ion Implantation

D. Tsvetanova, R. Vos, G. Vereecke, T. N. Parac-Vogt, F. Clemente,
K. Vanstreels, D. Radisic, T. Conard, A. Franquet, M. Jivanescu,
D. A. P. Nguyen, A. Stesmans, B. Brijs, P. Mertens, M. M. Heyns H785

Cu Retardation Performance of Extrinsic Gettering Layers in Thinned Wafers Evaluated by Transient Capacitance Measurement

K.-W. Lee, J.-C. Bea, T. Fukushima, T. Tanaka, M. Koyanagi H795

Low Temperature Synthesized Quaternary Chalcogenide $\text{Cu}_2\text{ZnSnS}_4$ from Nano-Crystallite Binary Sulfides

Y. Wang, H. Gong H800

Enhanced Efficiency of Polymer/ZnO Nanorods Hybrid Solar Cell Sensitized by CdS Quantum Dots

L. Wang, D. Zhao, Z. Su, B. Li, Z. Zhang, D. Shen H804

Microstructure Evolution of Sputtered Bi-Te Films during Post-Annealing: Phase Transformation and Its Effects on the Thermoelectric Properties

S.-J. Jeon, M. Oh, H. Jeon, S. D. Kang, H.-K. Lyeo, S. Hyun,
H.-J. Lee H808

Post Plasma Etch Residue Removal in Dilute HF Solutions

D. P. R. Thanu, S. Raghavan, M. Keswani H814

Performance Improved Mechanisms of Chlorine-Treated AlGaIn/GaN MOS-HEMTs with ZnO Gate Dielectric Layer

C.-T. Lee, Y.-L. Chiou H821

Chemical States of Copper Contaminants on SiO_2 Surfaces and Their Removal by ppm-order HCN Aqueous Solutions

M. Takahashi, Y. Higashi, S. Ozaki, H. Kobayashi H825

Fundamental Characteristics of Condensed Chemical Mechanical Polishing Waste Slurry

Y. Yamada, M. Kawakubo, S. Watanabe, T. Sugaya H830

Effect of Silicon Doped Quantum Barriers on Nitride-Based Light Emitting Diodes

T. H. Chiang, Y. Z. Chiou, S. J. Chang, T. K. Lin, S. P. Chang H836

Nickel Silicide Formation using Pulsed Laser Annealing for nMOSFET Performance Improvement

H.-Y. Chen, C.-Y. Lin, M.-C. Chen, C.-C. Huang, C.-H. Chien H840

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V. Janardhanam, J.-S. Kim, K. Moon, Y.-B. Lee, D.-G. Kim, S.-M. Kang, C.-J. Choi H846

Sensors and Displays: Principles, Materials, and Processing

Reduced Graphite Oxide-Indium Tin Oxide Hybrid Materials for use as a Transparent Electrode

K. S. Choi, Y. Park, K.-C. Kwon, J. Kim, C. K. Kim, S. Y. Kim, K. Hong, J.-L. Lee J231

Ca₅La₅(SiO₄)₃(PO₄)₃O₂:Ce³⁺, Mn²⁺: A Color-Tunable Phosphor with Efficient Energy Transfer for White-Light-Emitting Diodes

G. Zhu, Y. Wang, Z. Ci, B. Liu, Y. Shi, S. Xin J236

A Saturated Red-Emitting Phosphorescent Iridium(III) Complex for Application in Organic Light Emitting Diodes

L. Zhang, B. Li, L. Zhang, S. Yue, Q. Xue, S. Liu J243

Two-Step Synthesis of SrSi₂O₂N₂: Eu²⁺ Green Oxynitride Phosphor: Electron-Phonon Coupling and Thermal Quenching Behavior

Y.-C. Fang, P.-C. Kao, Y.-C. Yang, S.-Y. Chu J246

Intense Red-Emitting NaYSiO₄: Eu³⁺, Mo⁶⁺ Phosphors for White Light-Emitting Diodes

Y. Wen, Y. Wang, F. Zhang, B. Liu, Z. Zhao, J. Zhang, Z. Yang J250

Luminescence Properties of Ce³⁺-Activated SrLaGa₃S₆O and Application in White LEDs

R. Yu, B. Deng, G. Zhang, Y. An, J. Zhang, J. Wang J255

Luminescence of Eu²⁺ Ions in CsMgPO₄ Phosphor: Anomalous Emission and its Origin

Y. Huang, H. J. Seo J260

The Blue-Emitting Phosphor of Eu²⁺-Doped Ca₂Sr(PO₄)₂

X. Wang, F. Du, D. Wei, Y. Huang, H. J. Seo J264

Characteristics of A.C Electroluminescence in ZnGa₂O₄:Mn²⁺ Thin Film Devices

G. Anoop, K. M. Krishna, M. K Jayaraj J269

Nanostructured Materials, Carbon Nanotubes, and Fullerenes

Highly Conductive Ag Nanoparticulate Films Induced by Movable Rapid Thermal Annealing Applicable to Roll-to-Roll Processing

N.-R. Kim, J.-H. Lee, S.-M. Yi, Y.-C. Joo K165

Synthesis of Silica-Coated Ceria Particles for STI-CMP in a Single Step by Flame Spray Pyrolysis with an Emulsion

S. A. Song, S. B. Park K170

Interdisciplinary Topics

Electrowetting of Superhydrophobic ZnO Inverse Opals

L.-Y. Chen, C.-H. Lai, P.-W. Wu, S.-K. Fan P93

Self-Assembly of Amine Terminated Alkylthiol and Alkylidithiol Films on a Polycrystalline Copper Substrate

J. Denayer, J. Delhalle, Z. Mekbalif P100

Reviews

Critical Reviews in Electrochemistry and Solid-State Science and Technology CRES3T

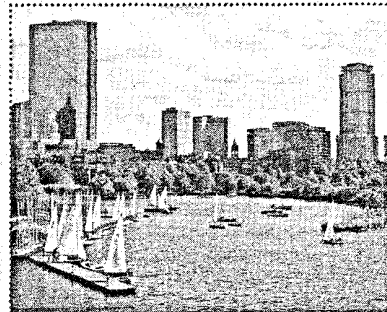
Progress in Flow Battery Research and Development

M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, M. Saleem R55

Erratum: Pt_xCo_y Catalysts Degradation in PEFC Environments:
Mechanistic Insights II. Preparation and Characterization of
Particles with Homogeneous Composition [*J. Electrochem.*
Soc., 157, B943 (2010)]

P. Fugier, S. Passot, C. Anglade, L. Guétaz, N. Guillet, E. De Vito,
S. Mailley, A. A. Franco S21

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Reductive Eliminations from Amido Metal Complexes: Implications for Metal Film Deposition

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The thermal decomposition of tetrakis(dimethylamido)titanium (TDMAT) follows a number of competitive reactions, including not only the known hydrogenation and β -hydride elimination steps, to produce dimethylamine and N-methylmethanimine respectively, but also a reductive elimination to yield tetramethylhydrazine and a more complex conversion to N,N,N',N'-trimethyldiaminomethane and N,N,N',N'-tetramethyldiaminomethane. The latter reactions may account for the reduction of the metal when these compounds are used for the atomic layer deposition (ALD) of metal nitride films. Similar reactions take place with tetrakis(ethylmethylamido)titanium (TEMAT) and with pentakis(dimethylamido)tantalum (PDMAT).

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Conformal films, that is, thin films that closely follow the shape of the underlying structures they cover, are crucial components in a variety of modern technologies,^{1–3} and particularly important in microelectronics, where they are used as conductor or insulator layers, and also as diffusion, adhesion, or protection barriers.^{4–6} In the past film growth for these applications has relied on physical deposition (PVD) methods,⁷ but those, being intrinsically directional, are ill suited for the requirements of modern electronic devices, which are now routinely prepared with sub-100 nm individual structures of very high aspect ratios and many narrow and deep holes and trenches.^{8,9} Chemical-based processes, which are isotropic, can better handle film deposition on rough surfaces.^{5,6,10}

Various chemical vapor deposition (CVD) methods have been developed over the years to address specific needs in different applications,¹¹ and particular excitement has developed recently around the idea of using a variation of CVD known as atomic layer deposition (ALD).^{9,12} In ALD, two self-limiting and complementary reactions are used sequentially and in alternating fashion to slowly build up solid films one monolayer at the time.^{13–16} ALD offers many advantages over other film growth processes:^{15,17} (1) the film thickness depends only on the number of cycles employed, not on the exposures used in each cycle (process control is simple and accurate); (2) there is less of a need for a homogeneous flux of the reactants through the reactor, a fact that makes processes reproducible and easy to scale for large-area coatings without sacrificing conformality; (3) it offers more flexibility in the design of the operational deposition conditions, requiring lower temperatures than regular CVD; (4) there is minimal or no interference from gas-phase reactions during the deposition process because of the separation of the two half reactions in time; and (5) it is easy to use for the manufacturing of layered structures.

On the negative side, ALD, like other CVD processes, suffers from some intrinsic limitations, in particular the fact that it may deposit undesirable contaminants within the growing films via side decomposition reactions of the precursors.^{18–20} This problem may in principle be addressed by choosing appropriate chemical precursors and deposition conditions, but that requires a good understanding of the surface chemistry involved. Little work has been carried out to provide that basic knowledge to date (although that is starting to change). Our laboratory has, in recent years embarked into a project to provide some insights into the details of the surface chemistry of key precursors for ALD.^{21–29} Here we provide a discussion on results obtained with the dialkylamido complexes often used in ALD of metal nitrides and metal oxides.

Thin metal nitride films are being considered as potential diffusion barriers for electrical interconnects. In the past electrical interconnects have been made out of aluminum, but more recently copper has drawn much attention because of its lower bulk resistivity and superior electromigration resistance.^{30,31} However, Cu reacts

with Si at relatively low temperatures; a diffusion barrier is needed to prevent the intermixing of the metal with the underlying elements of the device being made. This film needs to be thin and conformal, something that is increasingly more difficult to achieve with physical processes,³² and likely to be better produced by ALD instead.^{12,33} Transition metal nitrides are at present considered one of the most promising materials for this application, and dialkylamido complexes of the appropriate metals the most likely precursors for such ALD processes.^{15,17,34}

Although dialkylamido moieties can be as stable as their equivalent alkyl species, the thermal chemistry of dialkylamido metal complexes has been much less characterized than that of alkyl organometallics.³⁵ In fact, due to their weak metal-nitrogen bonds, only a handful of dialkylamido complexes are known with late transition metals. Dialkylamido compounds containing early transition metals are much more common, and have gained recent attention as convenient precursors for the deposition of metal, metal nitride, and metal oxide thin solid films.^{17,24,36} Nevertheless, the thermal conversion of those is also not well understood. They react readily with protic substrates to eliminate the original ligands as amines in a substitutional step, a transamination if the second reactant is another amine.^{37,38} They can also undergo a β -hydride elimination step from one of the dialkylamido ligands to form a coordinated imine^{25,37,39} and double bond insertion into metal-nitrogen bonds.³⁵ Interestingly, though, none of those reactions explain the reduction of the metal that occurs during the deposition of metal nitrides using early transition metal dialkylamido complexes. Here we report on a reductive elimination step from titanium and tantalum dialkylamido complexes that yields a substituted hydrazine and leaves behind a reduced metal center. A second more complex metal reducing reaction was also identified with diaminomethanes as the final products.

Experimental

The studies reported here relied on the use of gas chromatography/mass spectrometry (GC-MS) to analyze the gas products from thermal decomposition of the vapor of the dialkylamido compounds. The liquid compounds were introduced into a small (~10 ml) glass vial under nitrogen atmosphere, sealed with a Teflon/silicon septum, and heated to the desired temperature. Gas aliquots were then taken using a small syringe, and injected directly into the port of the GC-MS instrument (Agilent 7890/Waters GCT).²⁶ Surprisingly, we are not aware of other work in this area using such an approach, even though GC/MS is quite a powerful technique for the identification of products in gas-phase reactions.

Results and Discussion

A typical set of data from our GC/MS experiments is shown in Fig. 1, in this case for tetrakis(dimethylamido)titanium (TDMAT) heated to 425 K; reactivity was probed for a temperature range

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between 300 and 500 K, and the threshold for thermal conversion of TDMAT was identified at that temperature. Four products are seen in the gas chromatogram in Fig. 1 (main frame), each identifiable by its corresponding mass spectrum (insets): dimethylamine ($\text{HN}(\text{CH}_3)_2$, which shows as multiple peaks between 0.6 and 1.0 min), tetramethylhydrazine ($(\text{CH}_3)_2\text{N}-\text{N}(\text{CH}_3)_2$), N,N,N',N' -tetramethyldiaminomethane ($(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{N}(\text{CH}_3)_2$), and a fourth product with a mass spectrum quite similar to dimethylamine that we tentatively assign to N,N,N' -trimethyldiaminomethane ($\text{CH}_3\text{N}(\text{H})-\text{CH}_2-\text{N}(\text{CH}_3)_2$).

The first product, dimethylamine, originates from hydrogenation of the dimethylamido ligands, a reaction that has been well documented.^{40,41} Because in our experiments the amine is produced via decomposition of pure TDMAT, the extra hydrogen required for this hydrogenation step must originate from decomposition of other amido ligands within the same molecule. Preliminary work suggests that addition of either water or ammonia to the mixture increases the hydrogenation yield (data not shown).²⁶ Hydrogenation of amido ligands via reaction with ammonia has also been reported in the past.³⁷

The detection of tetramethylhydrazine, the second product, is novel, and the focus of this report. We suggest that this product originates from the reductive elimination of two dimethylamido ligands from a single metal center, via a direct nitrogen-nitrogen coupling reaction. More complex reactions are in principle possible: some low-valence metal dialkylamido compounds exist in dimeric form and disproportionate at relatively low temperatures,³⁵ and the formation of large oligomeric clusters have been reported with TDMAT.³⁷ In order to rule out such possibilities in our case, the stoichiometry of the reaction was determined by measuring reaction yields as a function of the TDMAT partial pressure in the reaction vial. Figure 2 shows the results. Linear dependences are seen for the production of both dimethylamine and tetramethylhydrazine with respect to the concentration of TDMAT in the gas phase, indicating the consumption of one single TDMAT molecule in both reactions per molecule of product produced. Deviations from this linear behavior are seen at high concentrations, but that is explained by the onset of condensation of the TDMAT in the vial (at 425 K, a concentration of 1 mmol/L is equivalent to approximately 25 Torr, close to the vapor pressure of TDMAT at that temperature).⁴² No solid products were observed in any of the experiments with the

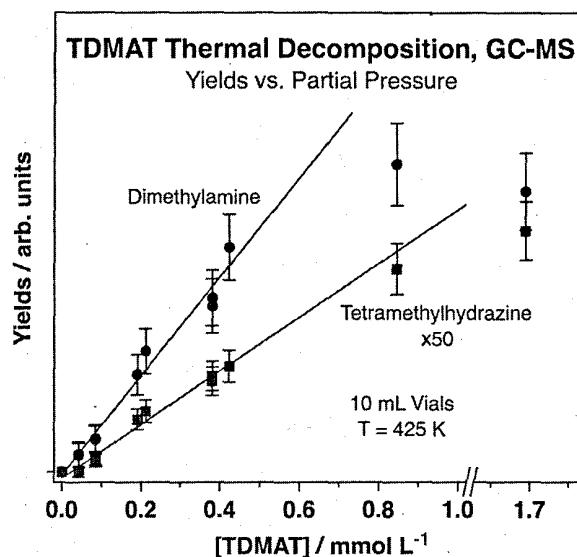


Figure 2. (Color online) Dependence of the yields for dimethylamine (blue circles) and tetramethylhydrazine (red squares) on the concentration of TDMAT in the gas phase.

pure dialkylamido complexes, a fact that also argues against polymerization reactions, although some solids and thin films on the walls of the vials were observed if water or ammonia were added to the reaction mixture. Finally, the contribution from surface-induced reactions was tested by additional experiments using silanized vials; those yielded the same products as in the experiments with the vials made out of regular glass.

There have been some reports of cross-coupling reactions between amido and alkyl ligands,^{43,44} of N-N coupling between amidinate ligands within a ruthenium complex,⁴⁵ and of the reverse oxidative addition of hydrazine to metal centers,^{46,47} but, to the best of our knowledge, ours is the first report of coupling of two amido ligands from a single metal organic compound. The chemistry reported here appears to be fairly general: analogous results were obtained with tetrakis(ethylmethylamido)titanium (TEMAT) and with pentakis(dimethylamido)tantalum (PDMAT) (data not shown). It was also determined that coupling to form hydrazine is inhibited by addition of either water or ammonia, at the expense of an increase in hydrogenation to the appropriate amine (dimethylamine with TDMAT).

The other two compounds identified in Fig. 1 are likely to be products of multiple-step reactions. We suggest that perhaps the

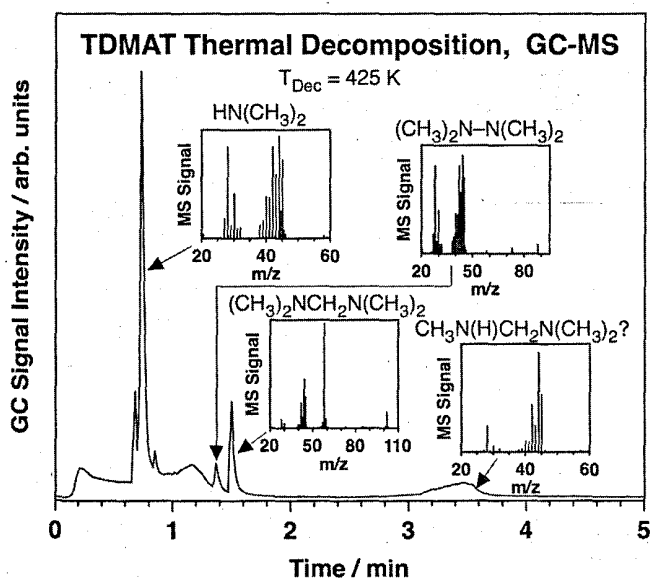


Figure 1. (Color online) GC/MS characterization of the gas-phase products obtained from thermal activation of TDMAT at 425 K. The main frame reports the GC trace, whereas the insets correspond to the mass spectra of the products identified by each GC peak.

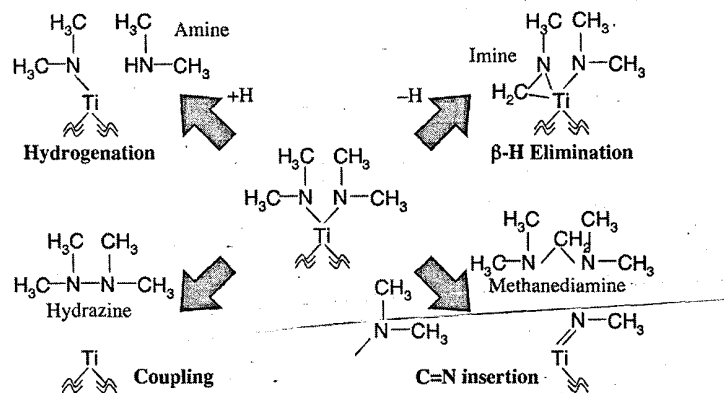


Figure 3. (Color online) Schematic representation of the proposed thermal chemistry of amido titanium and tantalum complexes on solid surfaces. This chemistry follows a complex set of reactions, including reductive coupling steps to produce hydrazines and diaminomethanes.

C=N bond in the imine produced by β -hydride elimination from one of the amido moieties may insert into the bond between the metal and a second amido ligand to form an (aminomethylene)amido, $-\text{N}(\text{CH}_3)\text{CH}_2\text{N}(\text{CH}_3)_2$, ligand.^{48,49} Hydrogenation of that new ligand would produce N,N,N',N' -trimethyldiaminomethane, the fourth product detected in the GC reported in Fig. 1. N,N,N',N' -tetramethyldiaminomethane, the third product, may be made via the transfer of a methyl group from one dimethylamido ligand to the amido nitrogen atom in $-\text{N}(\text{CH}_3)\text{CH}_2\text{N}(\text{CH}_3)_2$.⁵⁰ Limited precedent exists for all these steps, but no sufficient evidence could be obtained from our experiments to fully support this mechanism.

Conclusions

In summary, we report the formation of several products from thermal activation of titanium and tantalum dialkylamido complexes, including hydrazines and diamidomethanes, which are the result of newly identified reductive steps (Fig. 3). The reduction of the metal in these thermally-driven reactions is of relevance to their use for the deposition of metal nitride films. The formation of TiN from TDMAT, for instance, requires the conversion of Ti(IV) to Ti(III), and the reductive elimination of the dialkylamido ligands may be involved in that conversion. Typically, it is thought that metal nitride deposition with these compounds requires the use of a reducing agent, typically ammonia. Hydrazine formation via reductive elimination of dialkylamido ligands is certainly less favorable thermodynamically than reduction by ammonia, which presumably gets oxidized to produce molecular nitrogen.^{37,38} Nevertheless, the former reaction may be kinetically favored, in particular in atomic layer deposition (ALD), where the two half reactions (the exposure of the substrate to the metal precursor and to ammonia) are separated in time. We have recently reported evidence for the self-reduction of TiCl_4 in a similar ALD process with NH_3 .²¹⁻²³ It is also worth noting that in the studies reported here the self-reducing steps could be inhibited, at least in part, by addition of a second agent, either ammonia or water, to the mix.

Acknowledgments

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