

Title (en)

AN ELECTROCHEMICAL PROCESS FOR PRODUCING NANOPARTICLES OF CUPRATE HYDROXYCHLORIDES

Title (de)

ELEKTROCHEMISCHES VERFAHREN ZUR HERSTELLUNG VON NANOPARTIKELN VON CUPRAT-HYDROXYCHLORIDEN

Title (fr)

PROCÉDÉ ÉLECTROCHIMIQUE DE PRODUCTION DE NANOPARTICULES D'HYDROXYCHLORURES DE CUPRATE

Publication

EP 3674445 A1 20200701 (EN)

Application

EP 18248090 A 20181227

Priority

EP 18248090 A 20181227

Abstract (en)

The present invention relates to an electrochemical process for producing nanoparticles of mixed copper hydroxide-chloride compounds responding to the chemical formula $M_{x-y-z}Cu_{4-x}(OH)_yCl_z$ wherein M is one or more metal cations from the group comprising a divalent earth alkali metal cation, a divalent transition metal cation or a trivalent transition metal cation, and wherein $0 \leq x \leq 1$, $5.5 \leq y \leq 6.5$ and $1.5 \leq z \leq 3$, the method comprising the steps of (1) supplying to a cathode compartment of an electrochemical cell, wherein the cathode compartment comprises a catholyte and is equipped with a cathode comprising a gas diffusion electrode with a porous electrochemically active material, a liquid water based mixture containing dissolved therein Cl^- ions, at least one precursor salt containing the one or more metal cations M, and at least one Cu^{2+} precursor salt, wherein the ratio of the concentration of Cu^{2+} to M is smaller than 10:1, (2) adjusting the pH of the reaction mixture to a value between 2.0 and 6.0, (3) supplying an O_2 containing oxidant gas to the gas diffusion electrode, (4) subjecting the cathode to an electrochemical potential which is below the thermodynamic limit of O_2 reduction at the pH of the reaction mixture, (5) applying a potential to the gas diffusion electrode to cause reduction of the O_2 contained in the oxidant gas to one or more of the corresponding peroxide, OH^- , ionic and/or radical reactive O containing species, and isolating nanoparticles of $M_{x-y-z}Cu_{4-x}(OH)_yCl_z$.

IPC 8 full level

C25B 1/00 (2006.01); **C25B 1/30** (2006.01); **C25B 11/03** (2006.01)

CPC (source: EP)

C25B 1/01 (2021.01); **C25B 1/30** (2013.01); **C25B 9/19** (2021.01); **C25B 11/032** (2021.01); **C25B 13/07** (2021.01); **C25B 13/08** (2013.01)

Citation (applicant)

- US 2018023201 A1 20180125 - DOMINGUEZ BENETTON XOCHITL [BE], et al
- SHORES, M.; NYTKO, E.; BARTLETT, B.; NOCERA, D.: "A Structurally Perfect $S = 1/2$ Kagome Antiferromagnet", J. A. CHEM. SOC., vol. 127, no. 39, 2005, pages 13462 - 13463
- BALENTS, L.: "Spin Liquids in Frustrated Magnets", NATURE, vol. 464, no. 7286, 2010, pages 199 - 208
- COLMAN, R.; RITTER, C.; WILLS, A.: "Toward Perfection: Kapellasite, $CsZn(OH)Cl$, a New Model $S = 1/2$ Kagome Antiferromagnet", CHEM. MATER., vol. 20, no. 22, 2008, pages 2005 - 2007
- HAN, T.; HELTON, J.; CHU, S.; PRODI, A.; SINGH, D.; MAZZOLI, C.; MULLER, P.; NOCERA, D.; LEE, Y.: "Synthesis and Characterization of Single Crystals of the Spin-1/2 Kagome-Lattice Antiferromagnets $Zn_xCu_{1-x}OHCl$ ", PHYS. REV. B, vol. 83, no. 10, 2011, pages 100402 - 100406
- COLMAN, R. H.; SINCLAIR, A.; WILLS, A. S.: "Magnetic and Crystallographic Studies of Mg-Herbertsmithite, $y-CuS Mg(OH)Cl$ - A New $S = 1/2$ Kagome Magnet and Candidate Spin Liquid", CHEM. MATER., vol. 23, no. 7, 2011, pages 1811 - 1817
- SUN, W.; HUANG, Y. X.; PAN, Y.; MI, J. X.: "Strong Spin Frustration and Negative Magnetization in $LnCu(OH)Cl$ ($Ln = Nd$ and Sm) with Triangular Lattices: The Effects of Lanthanides", DALT. TRANS., vol. 46, no. 29, 2017, pages 9535 - 9541
- SUN, W.; HUANG, Y. X.; NOKHRIN, S.; PAN, Y.; MI, J. X.: "Perfect Kagome Lattices in $YC(OH)Cl$ s: A New Candidate for the Quantum Spin Liquid State", J. MATER. CHEM. C, vol. 4, no. 37, 2016, pages 8772 - 8777
- NORMAN, M. R.: "Colloquium: Herbertsmithite and the Search for the Quantum Spin Liquid", REV. MOD. PHYS., vol. 88, no. 4, 2016, pages 1 - 14
- HELTON, J. S.; MATAN, K.; SHORES, M. P.; NYTKO, E. A.; BARTLETT, B. M.; YOSHIDA, Y.; TAKANO, Y.; SUSLOV, A.; QIU, Y.; CHUNG, J. H.: "Spin Dynamics of the Spin-1/2 Kagome Lattice Antiferromagnet $ZnCu(OH)Cl$ ", PHYS. REV. LETT., vol. 98, no. 10, 2007, pages 3 - 6
- SHORES, M. P.; NYTKO, E. A.; BARTLETT, B. M.; NOCERA, D. G.: "A Structurally Perfect $S = 1/2$ Kagome Antiferromagnet", J. AM. CHEM. SOC., vol. 127, no. 39, 2005, pages 13462 - 13463
- WELCH, M. D.; SCIBERRAS, M. J.; WILLIAMS, P. A.; LEVERETT, P.; SCHLUTER, J.; MALCHEREK, T.: "A Temperature-Induced Reversible Transformation between Paratacamite and Herbertsmithite", PHYS. CHEM. MINER., vol. 41, no. 1, 2014, pages 33 - 48
- AIDOU, F.; ALDOUS, D.; GOFF, R.; SLAWIN, A.; ATTFIELD, J.; MORRIS, R.; LIGHTFOOT, P.: "An Ionothermally Prepared $S = 1/2$ Vanadium Oxyfluoride Kagome Lattice", NAT. CHEM., vol. 3, no. 10, 2011, pages 801 - 806
- HAN, T.-H.; HELTON, J. S.; CHU, S.; NOCERA, D. G.; RODRIGUEZ-RIVERA, J. A.; BROHOLM, C.; LEE, Y. S.: "Fractionalized Excitations in the Spin-Liquid State of a Kagome-Lattice Antiferromagnet", NATURE, vol. 492, no. 7429, 2012, pages 406 - 410
- ENGELBREKT, C.; MALCHO, P.; ANDERSEN, J.; ZHANG, L.; STAHL, K.; LI, B.; HU, J.; ZHANG, J.: " $C(OH)Cl$ and Tenorite CuO Nanoparticles by pH Control", J. NANOPARTICLE RES., vol. 16, no. 8, 2014, pages 2562
- VERMEIREN, P.; ADRIANSEN, W.; LEYSEN, R.: "Zirfon®: A New Separator for Ni-H Batteries and Alkaline Fuel Cells", INT. J. HYDROGEN ENERGY, vol. 21, no. 8, 1996, pages 679 - 684, XP000590122, DOI: doi:10.1016/0360-3199(95)00132-8
- AGUSTINI, D.; BERGAMINI, M. F.; MARCOLINO-JUNIOR, L. H.: "Low Cost Microfluidic Device Based on Cotton Threads for Electroanalytical Application", LAB CHIP, vol. 16, no. 2, 2016, pages 345 - 352
- BELSLY, A.; HELDERMAN, M.; KAREN, V. L.; ULKCH, P.: "New Developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in Support of Materials Research and Design", ACTA CRYSTALLOGR. SECT. B STRUCT. SCI., vol. 58, no. 3, 2002, pages 364 - 369
- GORBITZ, C. H.: "The Development and Use of a Crystallographic Database", ACTA CRYSTALLOGR. SECT. B STRUCT. SCI. CRYST. ENG. MATER., vol. 72, no. 2, 2016, pages 167 - 168
- SLJUKIC, B.; BANKS, C. E.; COMPTON, R. G.: "An Overview of the Electrochemical Reduction of Oxygen at Carbon-Based Modified Electrodes", J. IRAN. CHEM. SOC., vol. 2, no. 1, 2005, pages 1 - 25
- YANG, H.-H.; MCCREERY, R. L.: "Elucidation of the Mechanism of Dioxygen Reduction on Metal-Free Carbon Electrodes", J. ELECTROCHEM. SOC., vol. 147, no. 9, 2000, pages 3420
- SCHMIDT, M.; ZIMMER, F. M.; MAGALHAES, S. G.: "Spin Glass Induced by Infinitesimal Disorder in Geometrically Frustrated Kagome Lattice", PHYS. A STAT. MECH. ITS APPL., vol. 438, 2015, pages 416 - 423
- MERSMANN, A.; LOFFELMANN, M.: "Crystallization and Precipitation: The Optimal Supersaturation", CHEM. ENG. TECHNOL., vol. 23, no. 1, 2000, pages 11 - 15

- MALCHEREK, T.; SCHLUTER, J.: "Structures of the Pseudo-Trigonal Polymorphs of C (OH) Cl", ACTA CRYSTALLOGR. SECT. B STRUCT. SCI., vol. 65, no. 3, 2009, pages 334 - 341
- BRAITHWAITE, R. S. W.; MEREITER, K.; PAAR, W. H.; CLARK, A. M.: "Herbertsmithite, Cu Zn(OH) Cl , a New Species, and the Definition of Paratacamite", MINERAL. MAG., vol. 68, no. 3, 2004, pages 13
- BERTOLOTTI, G.; BERSANI, D.; LOTTICI, P. P.; ALESIANI, M.; MALCHEREK, T.; SCHLUTER, J.: "Micro-Raman Study of Copper Hydroxychlorides and Other Corrosion Products of Bronze Samples Mimicking Archaeological Coins", ANAL. BIOANAL. CHEM., vol. 402, no. 4, 2012, pages 1451 - 1457, XP035005093, DOI: doi:10.1007/s00216-011-5268-9
- KNELLER, E. F.; LUBORSKY, F. E.: "Particle Size Dependence of Coercivity and Remanence of Single-Domain Particles", J. APPL. PHYS., vol. 34, no. 3, 1963, pages 656 - 658
- RATT, F. L.; BAKER, P. J.; BLUNDELL, S. J.; LANCASTER, T.; OHIRA-KAWAMURA, S.; BAINES, C.; SHIMIZU, Y.; KANODA, K.; WATANABE, I.: "Magnetic and Non-Magnetic Phases of a Quantum Spin Liquid", NATURE, vol. 471, no. 7340, 2011, pages 612 - 616
- GALETTI, D.; PIMENTEL, B. M.; LIMA, C. L.; SILVA, E. C.: "Quantum Spin Tunneling of Magnetization in Small Ferromagnetic Particles", PHYS. A STAT. MECH. ITS APPL., vol. 388, no. 7, 2009, pages 1105 - 1110, XP025896687, DOI: doi:10.1016/j.physa.2008.12.044
- KOLHATKAR, A. G.; JAMISON, A. C.; LITVINOV, D.; WILLSON, R. C.; LEE, T. R.: "Tuning the Magnetic Properties of Nanoparticles", INT J MOL SCI, vol. 14, no. 8, 2013, pages 15977 - 6009
- ARTEAGA-CARDONA, F.; ROJAS-ROJAS, K.; COSTO, R.; MENDEZ-ROJAS, M. A.; HERNANDO, A.; DE LA PRESA, P.: "Improving the Magnetic Heating by Disaggregating Nanoparticles", J. ALLOYS COMPD., vol. 663, 2016, pages 636 - 644, XP029388476, DOI: doi:10.1016/j.jallcom.2015.10.285
- TOPKAYA, R.; AKMAN, O.; KAZAN, S.; AKTAS, B.; DURMUS, Z.; BAYKAL, A.: "Surface Spin Disorder and Spin-Glass-like Behaviour in Manganese-Substituted Cobalt Ferrite Nanoparticles", J. NANOPARTICLE RES., vol. 14, no. 10, 2012, pages 1156, XP035125678, DOI: doi:10.1007/s11051-012-1156-2
- NGO, A. T.; BONVILLE, P.; PILENI, M. P.: "Spin Canting and Size Effects in Nanoparticles of Nonstoichiometric Cobalt Ferrite", J. APPL. PHYS., vol. 89, no. 6, 2001, pages 3370 - 3376, XP012053133, DOI: doi:10.1063/1.1347001
- MARTINEZ, B.; OBRADORS, X.; BALCELLS, L.; ROUANET, A.; MONTY, C.: "Low Temperature Surface Spin-Glass Transition in γ -Fe₂O₃ Nanoparticles", PHYS. REV. LETT., vol. 80, 1998, pages 181 - 184
- ALIYU, H. D.; ALONSO, J. M.; DE LA PRESA, P.; POTTKER, W. E.; ITA, B.; GARCIA-HERNANDEZ, M.; HERNANDO, A., CHEM. MATER., 2018

Citation (search report)

- [I] US 2018023201 A1 20180125 - DOMINGUEZ BENETTON XOCHITL [BE], et al
- [I] US 2015200082 A1 20150716 - FUJIMARU ATSUSHI [JP], et al
- [X] US 2008171158 A1 20080717 - MADDAN ORVILLE LEE [US]
- [X] WEI SUN ET AL: "Perfect Kagomé lattice in YCu₃(OH)₆Cl₃: A new candidate for the quantum spin liquid state", 7 October 2016 (2016-10-07), XP055600976, Retrieved from the Internet <URL:http://www.rsc.org/suppdata/c6/tc/c6tc02399a/c6tc02399a1.pdf> [retrieved on 20190701]

Designated contracting state (EPC)

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated extension state (EPC)

BA ME

DOCDB simple family (publication)

EP 3674445 A1 20200701; EP 3674445 B1 20240417; EP 3674445 C0 20240417

DOCDB simple family (application)

EP 18248090 A 20181227