Complementary analyses of aging in a commercial LiFePO$_4$/graphite 26650 cell

In this work we investigate the electrode degradation mechanisms in a commercial 2.5 Ah LiFePO$_4$/graphite 26650 cylindrical cell. Aged and fresh electrode samples were prepared by cycling two cells respectively five and 22 k times. Subsequently the cells were disassembled in a glovebox and the electrode samples were prepared for electrochemical testing in a 3-electrode setup, and for characterization with XRD, XPS and low-kV FIB/SEM tomography. A 1 μm thick CEI (cathode electrolyte interface) layer was observed at the electrode/electrolyte interface of the aged LiFePO$_4$ electrode. Relative to the fresh LiFePO$_4$ electrode, the aged electrode exhibited a larger series resistance which indicates the observed degradation layer increases the ionic resistance. In addition, micron-sized agglomerates, probably a mixture of carbonaceous material and decomposition products from the electrolyte, were observed at the electrode/electrolyte interface of the aged graphite electrode. These layers may contribute significantly to the loss of lithium inventory (LLI) in the cell, and to the loss of active material (LAM) in the graphite electrode. Low-voltage FIB/SEM tomography was used to detect local charging effects of graphite particles in the carbon electrode, an effect of poor dissipation of the electric charge to the ground after the sample interaction with the electron beam. The charging effects were primarily observed in the aged electrode and most of the locally charged particles were found to be close to the electrode/electrolyte interface, indicating a poorly percolating graphite network near this interface.
Scopus rating (2015): CiteScore 4.86 SJR 1.321 SNIP 1.324
Web of Science (2015): Impact factor 4.803
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 4.59 SJR 1.378 SNIP 1.456
Web of Science (2014): Impact factor 4.504
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 4.44 SJR 1.427 SNIP 1.587
Web of Science (2013): Impact factor 4.086
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 3.99 SJR 1.644 SNIP 1.574
Web of Science (2012): Impact factor 3.777
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): CiteScore 4.15 SJR 1.615 SNIP 1.788
Web of Science (2011): Impact factor 3.832
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.685 SNIP 1.715
Web of Science (2010): Impact factor 3.65
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.523 SNIP 1.615
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 1.524 SNIP 1.458
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.551 SNIP 1.568
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.531 SNIP 1.726
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 1.484 SNIP 1.516
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 1.362 SNIP 1.567
Scopus rating (2003): SJR 1.637 SNIP 1.505
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 1.534 SNIP 1.441
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 1.312 SNIP 1.376
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 0.889 SNIP 1.161
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 0.936 SNIP 1.183
Original language: English
Keywords: Cathode electrolyte interface, Degradation mechanisms, Electrochemical impedance spectroscopy, Focused ion beam, Li-ion battery
DOIs: 10.1016/j.electacta.2018.07.124
Source: Scopus
Source-ID: 85050697400
Analysis of the Interphase on Carbon Black Formed in High Voltage Batteries

Carbon black (CB) additives commonly used to increase the electrical conductivity of electrodes in Li-ion batteries are generally believed to be electrochemically inert additives in cathodes. Decomposition of electrolyte in the surface region of CB in Li-ion cells at high voltages up to 4.9 V is here studied using electrochemical measurements as well as structural and surface characterizations. LiPF$_6$ and LiClO$_4$ dissolved in ethylene carbonate:diethylene carbonate (1:1) were used as the electrolyte to study irreversible charge capacity of CB cathodes when cycled between 4.9 V and 2.5 V. Synchrotron-based soft X-ray photoelectron spectroscopy (SOXPES) results revealed spontaneous partial decomposition of the electrolytes on the CB electrode, without applying external current or voltage. Depth profile analysis of the electrolyte/cathode interphase indicated that the concentration of decomposed species is highest at the outermost surface of the CB. It is concluded that carboxylate and carbonate bonds (originating from solvent decomposition) and LiF (when LiPF$_6$ was used) take part in the formation of the decomposed species. Electrochemical impedance spectroscopy measurements and transmission electron microscopy results, however, did not show formation of a dense surface layer on CB particles.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Applied Electrochemistry, Imaging and Structural Analysis, Uppsala University
Contributors: Younesi, R., Christiansen, A. S., Scipioni, R., Ngo, D., Simonsen, S. B., Edström, K., Hjelm, J., Norby, P.
Pages: A1289-A1296
Publication date: 2015
Peer-reviewed: Yes

Publication information
Journal: Journal of The Electrochemical Society
Volume: 162
Issue number: 7
ISSN (Print): 0013-4651
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 3.48 SJR 1.267 SNIP 1.009
Web of Science (2017): Impact factor 3.662
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.97 SJR 1.222 SNIP 0.963
Web of Science (2016): Impact factor 3.259
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 3.17 SJR 1.115 SNIP 1.066
Web of Science (2015): Impact factor 3.014
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 3.36 SJR 1.213 SNIP 1.25
Web of Science (2014): Impact factor 3.266
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 2.92 SJR 1.169 SNIP 1.309
Web of Science (2013): Impact factor 2.859
ISI indexed (2013): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 2.61 SJR 1.329 SNIP 1.281
Web of Science (2012): Impact factor 2.588
ISI indexed (2012): ISI indexed yes
Analysis of the Interphase on Carbon Black Formed in High Voltage Batteries

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited.

Electronic versions:
Analysis_of_the_Interphase.pdf

DOIs:
10.1149/2.0761507jes

Analysis of the Interphase on Carbon Black Formed in High Voltage Batteries

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Applied Electrochemistry, Imaging and Structural Analysis, Uppsala University
Contributors: Younesi, R., Christiansen, A. S., Scipioni, R., Ngo, D., Simonsen, S. B., Edström, K., Hjelm, J., Norby, P.
Number of pages: 1
Publication date: 2015
Capillary based Li-air batteries for *in situ* synchrotron X-ray powder diffraction studies

For Li-air batteries to reach their full potential as energy storage systems, a complete understanding of the conditions and reactions in the battery during operation is needed. To follow the reactions in situ a capillary-based Li-O2 battery has been developed for synchrotron-based *in situ* X-ray powder diffraction (XRPD). In this article, we present the results for the analysis of 1st and 2nd deep discharge and charge for a cathode being cycled between 2 and 4.6 V. The crystalline precipitation of Li2O2 only is observed in the capillary battery. However, there are indications of side reactions. The Li2O2 diffraction peaks grow with the same rate during charge and the development of the full width at half maximum (FWHM) is hkl dependent. The difference in the FWHM of the 100 and the 102 reflections indicate anisotropic morphology of the Li2O2 crystallites or defects along the c-axis. The effect of constant exposure of X-ray radiation to the electrolyte and cathode during charge of the battery was also investigated. X-ray exposure during charge leads to changes in the development of the intensity and the FWHM of the Li2O2 diffraction peaks. The X-ray diffraction results are supported by *ex situ* X-ray photoelectron spectroscopy (XPS) of discharged cathodes to illuminate non-crystalline deposited materials.
Charge Localization in the Lithium Iron Phosphate Li₃Fe₂(PO₄)₃ at High Voltages in Lithium-Ion Batteries
Possible changes in the oxidation state of the oxygen ion in the lithium iron phosphate Li₃Fe₂(PO₄)₃ at high voltages in lithium-ion (Li-ion) batteries are studied using experimental and computational analysis. Results obtained from synchrotron-based hard X-ray photoelectron spectroscopy and density functional theory (DFT) show that the oxidation state of O²⁻ ions is altered to higher oxidation states (O⁰⁻, δ<2) upon charging Li₃Fe₂(PO₄)₃ to 4.7 V.
Depth profiling the solid electrolyte interphase on lithium titanate (Li4Ti5O12) using synchrotron-based photoelectron spectroscopy

The presence of a surface layer on lithium titanate (Li4Ti5O12, LTO) anodes, which has been a topic of debate in scientific literature, is here investigated with tunable high surface sensitive synchrotron-based photoelectron spectroscopy (PES) to obtain a reliable depth profile of the interphase. Li||LTO cells with electrolytes consisting of 1 M lithium hexafluorophosphate dissolved in ethylene carbonate:diethyl carbonate (LiPF6 in EC:DEC) were cycled in two different voltage windows of 1.0-2.0 V and 1.4-2.0 V. LTO electrodes were characterized after 5 and 100 cycles. Also the pristine electrode as such, and an electrode soaked in the electrolyte were analyzed by varying the photon energies enabling depth profiling of the outermost surface layer. The main components of the surface layer were found to be ethers, P-O containing compounds, and lithium fluoride.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Uppsala University
Contributors: Nordh, T., Younesi, R., Brandell, D., Edström, K.
Number of pages: 7
Pages: 173-179
Publication date: 2015
Peer-reviewed: Yes

Publication information
Journal: Journal of Power Sources
Volume: 294
ISSN (Print): 0378-7753
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 7 SJR 2.202 SNIP 1.536
Web of Science (2017): Impact factor 6.945
Web of Science (2017): Indexed yes
Instability of Ionic Liquid-Based Electrolytes in Li−O2 Batteries

Ionic liquids (ILs) have been proposed as promising solvents for Li−air battery electrolytes. Here, several ILs have been investigated using differential electrochemical mass spectrometry (DEMS) to investigate the electrochemical stability in a Li−O2 system, by means of quantitative determination of the rechargeability (OER/ORR), and thereby the Coulombic efficiency of discharge and charge. None of the IL-based electrolytes are found to behave as needed for a functional Li−O2 battery but perform better than commonly used organic solvents. Also the extent of rechargeability/reversibility has been found to be strongly dependent on the choice of IL cation and anion as well as various impurities.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Fundamental Electrochemistry, Chalmers University of Technology
Number of pages: 7
Pages: 18084–18090
Publication date: 2015
Peer-reviewed: Yes
Early online date: 2015

Publication information
Journal: The Journal of Physical Chemistry Part C
Volume: 119
Issue number: 32
ISSN (Print): 1932-7447
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 4.58 SJR 2.135 SNIP 1.147
Web of Science (2017): Impact factor 4.484
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 4.48 SJR 1.964 SNIP 1.195
Web of Science (2016): Impact factor 4.536
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 4.68 SJR 1.886 SNIP 1.26
Web of Science (2015): Impact factor 4.509
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 5.08 SJR 2.032 SNIP 1.447
Web of Science (2014): Impact factor 4.772
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 5.14 SJR 2.143 SNIP 1.445
Web of Science (2013): Impact factor 4.835
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 4.98 SJR 2.529 SNIP 1.461
Web of Science (2012): Impact factor 4.814
ISI indexed (2012): ISI indexed yes
Presently lithium hexafluorophosphate ($\text{LiPF}_6$) is the dominant Li-salt used in commercial rechargeable lithium-ion batteries (LIBs) based on a graphite anode and a 3–4 V cathode material. While LiPF$_6$ is not the ideal Li-salt for every important electrolyte property, it has a uniquely suitable combination of properties (temperature range, passivation, conductivity, etc.) rendering it the overall best Li-salt for LIBs. However, this may not necessarily be true for other types of Li-based batteries. Indeed, next generation batteries, for example lithium–metal (Li–metal), lithium–oxygen (Li–O$_2$), and lithium–sulfur (Li–S), require a re-evaluation of Li-salts due to the different electrochemical and chemical reactions and conditions within such cells. This review explores the critical role Li-salts play in ensuring in these batteries viability.

**General information**

State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Uppsala University, Oak Ridge National Laboratory, Chalmers University of Technology, ALISTORE-ERI European Research Institute
Number of pages: 18
Pages: 1905-1922
Publication date: 2015
Peer-reviewed: Yes
Early online date: 2015

**Publication information**

Journal: Energy & Environmental Science
Issue number: 8
ISSN (Print): 1754-5692
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 30.87 SJR 14.59 SNIP 4.819
Plasma properties during magnetron sputtering of lithium phosphorous oxynitride thin films

The nitrogen dissociation and plasma parameters during radio frequency sputtering of lithium phosphorus oxynitride thin films in nitrogen gas are investigated by mass appearance spectrometry, electrostatic probes and optical emission spectroscopy, and the results are correlated with electrochemical properties and microstructure of the films. Low pressure and moderate power are associated with lower plasma density, higher electron temperature, higher plasma potential and larger diffusion length for sputtered particles. This combination of parameters favors the presence of more atomic nitrogen, a fact that correlates with a higher ionic conductivity. Despite of lower plasma density the film grows faster at lower pressure where the higher plasma potential, translated into higher energy for impinging ions on the substrate, resulted in a compact and smooth film structure. Higher pressures showed much less nitrogen dissociation and lower ion energy with thinner films, less ionic conductivity and poor film structure with large roughness.

General information
State: Published
Reduced graphene oxide for Li–air batteries: the effect of oxidation time and reduction conditions for graphene oxide

Reduced graphene oxide (rGO) has shown great promise as an air-cathode for Li-air batteries with high capacity. In this article we demonstrate how the oxidation time of graphene oxide (GO) affects the ratio of different functional groups and how trends of these in GO are extended to chemically and thermally reduced GO. We investigate how differences in functional groups and synthesis may affect the performance of Li-O-2 batteries. The oxidation timescale of the GO was varied between 30 min and 3 days before reduction. Powder X-ray diffraction, micro-Raman, FE-SEM, BET analysis, and XPS were used to characterize the GO's and rGO's. Selected samples of GO and rGO were analyzed by solid state C-13 MAS NMR. These methods highlighted the difference between the two types of rGO's, and XPS indicated how the chemical trends in GO are extended to rGO. A comparison between XPS and C-13 MAS NMR showed that both techniques can enhance the structural understanding of rGO. Different rGO cathodes were tested in Li-O-2 batteries which revealed a difference in overpotentials and discharge capacities for the different rGO's. We report the highest Li-O-2 battery discharge capacity recorded of approximately 60,000 mAh/gcarbon achieved with a thermally reduced GO cathode. (C) 2015 Elsevier Ltd. All rights reserved.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, University of Copenhagen, University of Southern Denmark, Uppsala University
Number of pages: 12
Pages: 233-244
Publication date: 2015
Peer-reviewed: Yes

Publication information
Journal: Carbon
Volume: 85
ISSN (Print): 0008-6223
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 6.76 SJR 2.226 SNIP 1.666
Web of Science (2017): Impact factor 7.082
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 6.49 SJR 2.091 SNIP 1.648
Web of Science (2016): Impact factor 6.337
A New Look at the Stability of Dimethyl Sulfoxide and Acetonitrile in Li-O2 Batteries

Dimethyl sulfoxide (DMSO) and acetonitrile (MeCN) have recently been highlighted as promising electrolyte solvents for Li-O2 batteries. Possible reactions between these two solvents and Li2O2 are here discussed using X-ray photoelectron spectroscopy to analyze surface of the Li2O2 powder after direct contact with the solvents for different times of exposure. The results indicated that Li2O2 decomposes DMSO solvents, whereas no indication of degradation of MeCN by Li2O2 was observed.

© 2014 The Electrochemical Society.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials
Contributors: Younesi, R., Norby, P., Vegge, T.
Pages: A15-A18
Publication date: 2014
Peer-reviewed: Yes

Publication information
Journal: ECS Electrochemistry Letters
Volume: 3
ISSN (Print): 1099-0062
Ratings:
Scopus rating (2017): SJR 0.688 SNIP 0.819
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.76 SJR 0.631 SNIP 0.78
Web of Science (2016): Impact factor 1.771
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 1.97 SJR 0.767 SNIP 0.685
Web of Science (2015): Impact factor 1.962
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 1.77 SJR 0.643 SNIP 0.771
Web of Science (2014): Impact factor 2.321
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 1.48 SJR 0.639 SNIP 0.696
Web of Science (2013): Impact factor 2.149
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.068 SNIP 1.006
Web of Science (2012): Impact factor 2.01
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.056 SNIP 0.984
Web of Science (2011): Impact factor 1.995
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.183 SNIP 1.01
Web of Science (2010): Impact factor 1.981
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.231 SNIP 1.003
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Batteries: an important piece in the puzzle of renewable energies for a better world

Along with the rapid growth in the world population, the concerns regarding the production and consumption of energy originating from fossil fuels have been increasing in recent years. Therefore, there is higher demand to develop “clean” renewable energies to reduce the use of fossil fuel.

Communication: The influence of CO₂ poisoning on overvoltages and discharge capacity in non-aqueous Li-Air batteries

The effects of Li₂CO₃ like species originating from reactions between CO₂ and Li₂O₂ at the cathode of non-aqueous Li-air batteries were studied by density functional theory (DFT) and galvanostatic charge-discharge measurements. Adsorption energies of CO₂ at various nucleation sites on a stepped (1¯100) Li₂O₂ surface were determined and even a low concentration of CO₂ effectively blocks the step nucleation site and alters the Li₂O₂ shape due to Li₂CO₃ formation. Nudged elastic band calculations show that once CO₂ is adsorbed on a step valley site, it is effectively unable to diffuse
and impacts the Li2O2 growth mechanism, capacity, and overvoltages. The charging processes are strongly influenced by CO2 contamination, and exhibit increased overvoltages and increased capacity, as a result of poisoning of nucleation sites: this effect is predicted from DFT calculations and observed experimentally already at 1% CO2. Large capacity losses and overvoltages are seen at higher CO2 concentrations. © 2014 AIP Publishing LLC.
High Voltage Surface Degradation on Carbon Blacks in Lithium Ion Batteries

In order to increase the power density of Li-ion batteries, much research is focused on developing cathode materials that can operate at high voltages above 4.5 V with a high capacity, high cycling stability, and rate capability. However, at high voltages all the components of positive electrodes including carbon black (CB) additives have a potential risk of degradation. Though the weight percentage of CB in commercial batteries is generally very small, the volumetric amount and thus the surface area of CB compose a rather large part of a cathode due to its small particle size (≈ 50 nm) and high surface area. In this work, the performance of Super P in Li-ion cells at high voltages up to 4.9 V is studied using electrochemical measurements as well as surface characterizations.

Influence of annealing temperature on the electrochemical and surface properties of the 5-V spinel cathode material LiCr$_{0.2}$Ni$_{0.4}$Mn$_{1.4}$O$_4$ synthesized by a sol-gel technique
LiCr$_{0.2}$Ni$_{0.4}$Mn$_{1.4}$O$_4$ was synthesized by a sol–gel technique in which tartaric acid was used as oxide precursor. The synthesized powder was annealed at five different temperatures from 600 to 1,000 °C and tested as a 5-V cathode material in Li-ion batteries. The study shows that annealing at higher temperatures resulted in improved electrochemical performance, increased particle size, and a differentiated surface composition. Spinel powders synthesized at 900 °C had initial discharge capacities close to 130 mAh g$^{-1}$ at C and C/2 discharge rates. Powders synthesized at 1,000 °C showed capacity retention values higher than 85 % at C/2, C, and 2C rates at 25 °C after 50 cycles. Annealing at 600–800 °C resulted in formation of spinel particles smaller than 200 nm, while almost micron-sized particles were obtained at 900–1,000 °C. Chromium deficiency was detected at the surface of the active materials annealed at low temperatures. The XPS results indicate presence of Cr$^{6+}$ impurity when the annealing temperature was not high enough. The study revealed that increased annealing temperature is beneficial for both improved electrochemical performance of LiCr$_{0.2}$Ni$_{0.4}$Mn$_{1.4}$O$_4$ and for avoiding formation of Cr$^{6+}$ impurity on its surface.
In Situ Synchrotron XRD on a Capillary Li-O₂ Battery Cell

In situ studies give an opportunity to explore systems with a minimum of external interference. As Li-air batteries hold the promise for a future battery technology the investigation of the discharge and charge components of the cathode and anode is of importance, as these components may hold the key to making a large capacity rechargeable battery[1].

Different design for in situ XRD studies of Li-O₂ batteries has been published, based on coin cell like configuration[2] [3] or Swagelok designs [4]. Capillary batteries have been investigated for the Li-ion system since its development[5], but no capillary batteries of Li-air has yet been designed. Some of the advantage of the capillary battery design lies in its ability to separate the cathode and anode and avoid the use of glass fiber or separators, which may enable ex situ analysis of battery components. The battery design consist of a electrolyte filled capillary with anode and cathode in each end suspended on stainless steel wires, the oxygen in-let is placed on the cathode side of the battery with a flushing system for oxygen in-let. In this study we present a flexible design of a capillary based Li-O₂ battery with discharge and charge investigated in dimethxyethane (DME) with synchrotron XRD. The in situ study in these batteries show clearly how Li₂O₂ precipitates on the cathode side of the battery during discharge (see Figure), as the Li₂O₂ reflections at 21.2°, 22.5° and 37.1° grows. The reflection at 27.8, 28.4 and 32.16 is from a stainless steel wire where the cathode is attached. The in situ XRD measurements show how the Li₂O₂ growth depend on current discharge rate and how the FWHM changes dependent on reflection and charge/discharge. Several cells were tested both ex situ and in situ, and in situ XRD for 1st discharge/charge and 2nd discharge/charge of the battery cell were measured, to give a better understanding of the electrochemistry in the Li-O₂battery. 1. Girishkumar, G., et al.. The Journal of Physical Chemistry Letters, 2010. 1(14): p. 2193-2203. 2. Lim, H., E. Yilmaz, and H.R. Byon, The Journal of Physical Chemistry Letters, 2012. 3(21): p. 3210-3215. 3. Ryan, K.R., et al., Journal of Materials Chemistry A, 2013. 1(23): p. 6915-6919. 4. Shui, J.-L., et al., Nat Commun, 2013. 4. 5. Johnsen, R.E. and P. Norby,. Journal of Applied Crystallography, 2013. 46(6): p. 1537-1543. [Formula]
Investigating Surface and Interface Phenomena in LiFeBO₃ Electrodes Using Photoelectron Spectroscopy Depth Profiling

The formation of surface and interface layers at the electrodes is highly important for the performance and stability of lithium ion batteries. To unravel the surface composition of electrode materials, photoelectron spectroscopy (PES) is highly suitable as it probes chemical surface and interface properties with high surface sensitivity. Additionally, by using synchrotron-generated hard x-rays as excitation source, larger probing depths compared to in-house PES can be achieved. Therefore, the combination of in-house soft x-ray photoelectron spectroscopy and hard x-ray photoelectron spectroscopy (HAXPES) enables reliable and non-destructive depth profiling. Thus, detailed investigation of compositional gradients at electrode surfaces and interfaces from a sub-monolayer to several nanometer length scales can be performed. As this depth region is especially relevant for both electronic and ionic transport processes, the presented combinatorial approach is a very valuable tool in characterizing battery electrodes and their interfaces. We apply this technique to lithium iron borate (LiFeBO₃) battery electrodes at different cycling conditions to study the surface and interface layer evolution. Due to its high theoretical capacity (220 mAh g⁻¹) LiFeBO₃ is a promising cathode material for lithium ion batteries. However, its application is limited because of significant degradation due to surface reactions upon exposure to moisture and air. Therefore, detailed compositional characterization of LiFeBO₃ electrode surfaces is essential to gain further understanding of the degradation processes. To study these properties for the pristine material, the electrode fabrication conditions were carefully controlled to limit contact to air and moisture. The investigation of the iron valence state in dependence of the electrode preparation as well as cycling conditions is presented as higher valence states of iron are most likely involved in the degradation process.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Uppsala University, Helmholtz-Zentrum Berlin für Materialien und Energie, Helmholtz Institute Ulm
Contributors: Maibach, J., Younesi, R., Schwarzburger, N., Gorgoi, M., Fichtner, M., Edström, K.
Number of pages: 1
Pages: 242
Publication date: 2014
Peer-reviewed: Yes

Ionic conductivity and the formation of cubic CaH₂ in the LiBH₄–Ca(BH₄)₂ composite
LiBH₄–Ca(BH₄)₂ composites were prepared by ball milling. Their crystal structures and phase composition were investigated using synchrotron X-ray diffraction and Rietveld refinement, and their ionic conductivity was measured using impedance spectroscopy. The materials were found to form a physical mixture. The composites were composed of α-Ca(BH₄)₂, γ-Ca(BH₄)₂ and orthorhombic LiBH₄, and the relative phase quantities of the Ca(BH₄)₂ polymorphs varied significantly with LiBH₄ content. The formation of small amounts of orthorhombic CaH₂ and cubic CaH₂ in a CaF₂-like structure was observed upon heat treatment. Concurrent formation of elemental boron may also occur. The ionic conductivity of the composites was measured using impedance spectroscopy, and was found to be lower than that of ball milled LiBH₄. Electronic band structure calculations indicate that cubic CaH₂ with hydrogen defects is electronically conducting. Its formation along with the possible precipitation of boron therefore has an effect on the measured conductivity of the LiBH₄–Ca(BH₄)₂ composites and may increase the risk of an internal short-circuit in the cells.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Institute for Energy Technology
Contributors: Sveinbjörnsson, D. P., Blanchard, D., Mýrdal, J. S. G., Younesi, R., Viskinde, R., Riktor, M. D., Norby, P., Vegge, T.
Nickel oxide crystalline nano flakes: synthesis, characterization and their use as anode in lithium-ion batteries

Nickel oxide crystalline nano flakes (NONFs)—only about 10 nm wide—were produced using a simple and inexpensive chemistry method followed by a short annealing in ambient air. In a first step, Ni(OH)2 sheets were synthesized by adding sodium hydroxide (NaOH) drop-wise in a Ni(NO3)2 aqueous solution that was then sonicated for up to 60 min, washed and vigorously stirred overnight in deionized water. In a second step, the products of this reaction were annealed in ambient air in the temperature range 285–450 °C producing the desired NONFs. The products were characterized using x-ray diffraction, scanning electron microscopy and high resolution transmission electron microscopy including electron diffraction and electron energy-loss spectroscopy. Electrochemical investigations showed that anodes made of these NONFs provided significantly higher discharge capacities (70 to 100% higher) compared to commercial nanometric NiO nanopowder used under the same conditions. Moreover, these NONFs had higher initial capacity retentions at both low and high current densities compared to the same NiO nanopowder.
Synthesis of tungsten oxide nanoparticles using a hydrothermal method at ambient pressure

Tungsten oxide (WO₃) nanostructures receive sustained interest for a wide variety of applications, and especially for its usage as a photocatalyst. It is therefore important to find suitable methods allowing for its easy and inexpensive large scale production. Tungstite (WO₃ center dot H₂O) nanoparticles were synthesized using a simple and inexpensive low temperature and low pressure hydrothermal (HT) method. The precursor solution used for the HT process was prepared by adding hydrochloric acid to diluted sodium tungstate solutions (Na₂WO₄ center dot 2H₂O) at temperatures below 5 degrees C and then dissolved using oxalic acid. This HT process yielded tungstite (WO₃ center dot H₂O) nanoparticles with the orthorhombic structure. A heat treatment at temperatures at or above 300 degrees C resulted in a phase transformation to monoclinic WO₃, while preserving the nanoparticles morphology. The production of WO₃ nanoparticles using this method is therefore a three step process: protonation of tungstate ions, crystallization of tungstite, and phase transformation to WO₃. Furthermore, this process can be tailored. For example, we show that WO₃ can be doped with cesium and that nanorods can also be obtained. The products were characterized using powder x-ray diffraction, transmission electron microscopy (including electron energy-loss spectroscopy and electron diffraction), and x-ray photoelectron spectroscopy.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, University of Puerto Rico
Contributors: Ahmadi, M., Younesi, R., Guinel, M. J.
Pages: 1424-1430
Publication date: 2014
Peer-reviewed: Yes

Publication information
Journal: Journal of Materials Research
Volume: 29
Issue number: 13
ISSN (Print): 0884-2914
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 1.55 SJR 0.61 SNIP 0.661
Web of Science (2017): Impact factor 1.495
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.51 SJR 0.651 SNIP 0.664
Web of Science (2016): Impact factor 1.673
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 1.48 SJR 0.638 SNIP 0.718
Web of Science (2015): Impact factor 1.579
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 1.8 SJR 0.811 SNIP 0.948
Web of Science (2014): Impact factor 1.647
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 1.77 SJR 0.832 SNIP 0.835
Web of Science (2013): Impact factor 1.815
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 1.57 SJR 0.92 SNIP 0.985
Web of Science (2012): Impact factor 1.713
ISI indexed (2012): ISI indexed yes
WO3 nano-ribbons: their phase transformation from tungstite (WO3·H2O) to tungsten oxide (WO3)

Tungsten oxide (WO3) nano-ribbons (NRs) were obtained by annealing tungstite (WO3·H2O) NRs. The latter was synthesized below room temperature using a simple, environmentally benign, and low cost aging treatment of precursors made by adding hydrochloric acid to diluted sodium tungstate solutions (Na2WO4·2H2O). WO3 generates significant interests and is being used in a growing variety of applications. It is therefore important to identify suitable methods of production and better understand its properties. The phase transformation was observed to be initiated between 200 and 300 °C, and the crystallographic structure of the NRs changed from orthorhombic WO3·H2O to monoclinic WO3. It was rigorously studied by annealing a series of samples ex situ in ambient air up to 800 °C and characterizing them afterward. A temperature-dependent Raman spectroscopy study was performed on tungstite NRs between minus 180 and 700 °C. Also, in situ heating experiments in the transmission electron microscope allowed for the direct observation of the phase transformation. Powder X-ray diffraction, electron diffraction, electron energy-loss spectroscopy, and X-ray photoelectron spectroscopy were employed to characterize precisely this transformation.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, University of Puerto Rico
Contributors: Ahmadi, M., Sahoo, S., Younesi, R., Gaur, A. P. S., Katiyar, R. S., Guinel, M. J.
Pages: 5899-5909
Publication date: 2014
Peer-reviewed: Yes

Publication information
Journal: Journal of Materials Science
Chemical stability of DMSO and ACN solvents in contact with Li$_2$O$_2$

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials
Contributors: Younesi, R., Norby, P., Vegge, T.
Publication date: 2013
Peer-reviewed: Yes

Publication information
Journal: Electrochemical Society. Meeting Abstracts (Online)
Volume: MA2013-02
Issue number: 9
Article number: 473
ISSN (Print): 2151-2043
Original language: English
Source: dtu
Source-ID: n::oai:DTIC-ART:highwire/390583836::34975
Research output: Research - peer-review > Conference abstract in journal – Annual report year: 2013

Combined DFT and Dems Study On the Role of CO2 Poisoning On the Electronic Conduction and Overpotentials in Li-Air Batteries

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials, Fundamental Electrochemistry
Pages: 412-412
Publication date: 2013
Peer-reviewed: Yes

Publication information
Journal: Electrochemical Society. Meeting Abstracts (Online)
Issue number: 9
Article number: MA2013-02
ISSN (Print): 2151-2043
Original language: English
Source: dtu
Source-ID: n::oai:DTIC-ART:highwire/390583775::31202
Research output: Research - peer-review > Conference abstract in journal – Annual report year: 2013

Reduced Graphene Oxide for Li-Air Batteries: The Effect of Oxidation Time and Reduction Conditions for Graphene Oxide

General information
The Influence of CO2 Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries

General information
State: Published
Organisations: Center for Atomic-scale Materials Design, Department of Energy Conversion and Storage, Atomic scale modelling and materials, Department of Physics, Fundamental Electrochemistry, Applied Electrochemistry
Number of pages: 1
Publication date: 2013
Peer-reviewed: No
Electronic versions:
The_Influence_of_CO2_Poisoning.pdf
Source: dtu
Source-ID: u::9953
Research output: Research › Poster – Annual report year: 2013

The Lithium-Air Battery: How Difficult Is to Make It Rechargeable?

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic scale modelling and materials
Contributors: Younesi, R.
Number of pages: 1
Publication date: 2013
Peer-reviewed: Yes
Electronic versions:
The_Lithium_Air_Battery.pdf
Source: dtu
Source-ID: u::9755
Research output: Research › peer-review › Conference abstract for conference – Annual report year: 2013

X-Ray Acceleration On Electrochemical Reaction

General information
State: Published
Organisations: Uppsala University
Contributors: Liu, J., Roberts, M., Younesi, R., Dahbi, M., Zhu, J., Gustafsson, T., Edström, K.
Number of pages: 1
Pages: 2458-2458
Publication date: 2013
Peer-reviewed: Yes