Anode Materials for Rechargeable Li-Ion Batteries

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Progress Report
(covering work through Jan 15, 2000 to Jan 14, 2001)

for the

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from

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1. Facilities and Personnel

This research is on materials for anodes and cathodes in electrochemical cells. The work is a mix of electrochemical measurements and analysis of the materials by transmission electron microscopy and x-ray diffractometry. At present, our experimental work involves only materials for Li storage, but we have been writing papers from our previous work on hydrogen-storage materials.

We have improved our infrastructure for electrochemical measurements at Caltech. We have in place a fabrication facility for making coin cells, and we have evaluated two different battery cyclers. We expect to purchase a unit in the next month or so. Sample preparation for the electron microscopy and x-ray diffractometry work is now routine. Although we are now making in-situ x-ray diffraction measurements on thin-film solid state cells in collaboration with our JPL colleagues, we have not yet performed in-situ measurements on operating coin cells. This is under development.

In personnel issues, two Ph.D. students completed their thesis successfully under this grant in 2000. Dr. Yun Ye, whose thesis was on hydrogen storage in novel carbon materials, is now working for a software company, Sybex, Inc. Adrian Hightower defended successfully his Ph.D. thesis on the electronic structure of Li-storage materials, and is now working for a startup company in Pasadena (Nanostream, Inc.). Although her arrival was delayed until the late summer of 2000 owing to visa problems,[*] Dr. Heike Gabrisch is now working as a postdoctoral fellow on the TEM parts of the research. Mr. Jason Graetz passed his candidacy examination in May 2000, and is now working full time on his thesis research under this grant. In August we were joined by Dr. Rachid Yazami (arguably the inventor of intercalated graphite for Li batteries), is spending a ~year sabbatical at Caltech away from his position at CNRS in Grenoble. His salary is paid primarily by CNRS, but Rachid has been a big help to this DOE research. One of his graduate students from Grenoble will be spending 4-5 months at Caltech starting in March 2001. There is a plan for Mark Obrovac, a Ph.D. sudent with Jeff Dahn in Dalhousie Univ., to start as a postdoc in the late summer of 2001.

In a looser collaboration, Peter Rez, a theoretical physicist at Arizona State University, has been performing electronic structure calculations to help us interpret some of the spectroscopy work. Likewise the former students Charles Witham (now at JPL) and Adrian Hightower are involved in writing up some of the results from, or evolving immediately out of, their Ph.D. thesis research.

[*] The cap on H1B visas was missed, but Heike qualified for an "O" or "outstanding scientist" visa.

2. Research Results

Our materials studies on electrode materials divide into electronic studies of the valence at and around Li atoms, and the crystal structures of these materials. We are addressing the basic questions of how these change with Li concentration, and what long-term changes take place during charge/discharge cycling of the materials.

Graphite Anodes -- Electronic structure

As part of his Ph.D. thesis research, Adrian Hightower has shown from the Li K-edge structure in electron energy loss spectrometry (EELS), that Li intercalated into carbon is neutral Li atoms, not Li ions. It turns out that a recent electronic structure calculation paper obtained the same result (the Li is only 5% ionic), but these results were presented in a way that allowed misinterpretation byt the electrochemical community. Indeed, the name "Li-ion" battery is incorrect.

Graphite Anodes -- Crystal Structure

A considerable amount of previous work has been performed on the structure of Li-graphite intercalation compounds, and on the types of disorder that exist in carbons and grahite. In collaboration with Rachid Yazami, we reacted molten Li with carbon single wall nano-tubes. The tube structure is destroyed, and we obtained an unusual compound of LiC_8. This novel ordered structure could be related to the small sizes of the compound. To our surprise, we have now observed LiC_8 in graphite charged in electrochemical cells. It seems that this unusual intercalation compound occurs near edges of the graphite crystal, but this is under further investigation.

$LiCoO_2$ Cathodes -- Electronic structure

We have measured the changes during lithiation of $LiCoO_2$ in EELS spectra of the Co $L_{2,3}$-edge and the O K-edge. The O K-edge shows a distinct pre-peak associated with unoccupied orbitals. The intensity of this pre-peak is filled as Li is added to the material, indicating that there is a transfer of electron from Li to the O. The changes are smaller at the the Co $L_{2,3}$-edge. Peter Rez has performed some electronic structure calculations that seem reasonably consistent with the changes at the O K-edge. He has, however, arranged to use the results from Gerd Ceder's group at MIT to calculate the changes with lithiation. These results from the Vienna VASP code are more reliable than our preliminary calculations because they include account for changes in structural relaxation and local disorder with changes in Li concentration.

$LiCoO_2$ Cathodes -- Crystal Structure

We have some evidence for spatial heterogeneity in electronic structure of the O K-edge. In materials partially depleted of Li it seems that some regions are altered more than others. This may correlate to defects in the microstructure.

Our effort now is to understand the character of structural defects in $LiCoO_2$. Dislocations and other defects are well known in this material, but their structure is not. We have a workinghypothesis that hexagonal $LiCoO_2$ has a similar set of structural defects as in graphite. The basal planes of grapene layers are often rotated or terminate within a crystal structure. We think that the OCoO layers in $LiCoO_2$ may have a similar type of disorder.

Hydrogen Storage Materials

As part of her Ph.D. thesis research, Dr. Yun Ye had studied hydrogen adsorption on a number of novel carbon materials. In earlier work we had reported a phase transition in carbon single wall nanotubes where under high hydrogen pressure and low temperature, the change in chemical potential of hydrogen molecules upon adsorption was sufficient to overcome the van der Waals attraction of the tubes to each other. The subsequent separation of the tubes exposed a large surface area for adsorption by hydrogen gas. Earlier in 2000 we had found the same behavior in fullerite, an impure mixture of C_{60} and C_{70}. We have also obtained some odd results on hydrogen adsorption by carbons with nanoparticle transition metal catalysts, but this work is not continuing.

Early in 2000 we completed a neutron small angle scattering experiment to measure the distribution of hydrogen in $LaNi_5$ and $LaNi_5$-Sn. The latter material has superior cycle life, perhaps caused by a smaller tendency towards pulverization, or decrepitation. The neutron scattering on deuterated materials showed that the hydrogen distribution is much more homogeneous in the $LaNi_5$-Sn, suggesting that Sn atoms reduce the internal strain gradients during hydriding.

3. Plans for 2001

Anode Materials

We are starting to use transmission electron microscopy to find the locations of Li atoms in graphites. The issues of interest are the apparent heterogeneities in the Li concentration, and the appearance of the novel intercalation compound LiC_8. Diffraction contrast from Li atoms has proved to be adequate for imaging work.

Cathodes

We are interested in heterogeneities in the Li concentration in $LiCoO_2$. More systematic work is planned to sort out their sizes, shapes, and possible relationship to structural defects in $LiCoO_2$.

Our colleages at JPL are preparing cathode materials of $Li(Ni,Co)O_2$ materials. The Ni $L_{2,3}$ edge will be interesting to compare to that of the Co $L_{2,3}$ edge at various states of lithiation.

Michael Thackeray and I have been talking about Mn-oxide cathodes, and the prospect of sorting out the electron structures in Mn-oxide cathodes. The Mn L-edge, and the O K-edge show considerable amount of structure in various compounds. We are trying to plan a collaboration to study them in Mn-oxide cathodes of various states of charge and cycling.

Thin Film Cells

We have begun to measure the internal stresses in thin film cells. The cells are operated in-situ in an x-ray diffractometer (at present discharged through a resistor). We believe we can test the heterogeneity of the internal stresses in the cathodes. The system seems to work, but we do not have results yet.

4. Publications acknowledging support of this grant

Patents

1. Ratnakumar V. Bugga, Brent Fultz, Robert C. Bowman, Jr.,
   Subbarao Surampudi, Charles Witham, and Adrian Hightower,
   "$LaNi_5$-Based Metal Hydride Electrode in Ni-MH Rechargeable Cells"
   U.S. Patent No. 5,888,665 issued March 30, 1999.

2. I. E. Anderson, T. W. Ellis, R. C. Bowman, Jr. C. Witham, B. Fultz,
   and B. V. Ratnakumar, "Ultrafine Hydrogen Storage Powders"
   U.S. Patent No. 6,074,453 issued June 13, 2000.

Ph.D. Theses

3. Adrian Hightower, "Lithium Electronic Environments in Rechargeable Battery Electrodes", Ph.D. in Materials Science, California Institute of Technology, July 14, 2000.

4. Yun Ye, "Interaction of Hydrogen with Novel Carbon Materials", Ph.D. in Materials Science, California Institute of Technology, August 8, 2000.

Publications

5. Y. Ye, C. C. Ahn, C. K. Witham, B. Fultz, J. Liu, A. Rinzler, D. Colbert, K. Smith and R. Smalley, “Hydrogen Adsorption by Single-Walled Carbon Nanotubes and their Cohesive Energy”, Appl. Phys. Lett., 74 (1999) p. 2307-2309.

6. A. Hightower, P. Delcroix, G. Le Caër, C-K. Huang, B. V. Ratnakumar,C. C. Ahn, and B. Fultz, “A ^{119}Sn Mössbauer Spectrometry Study of Li-SnO Anode Materials for Li-ion Cells”, J. Electrochem. Soc. 147 (2000) p. 1-8.

7. M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. C. Ahn and B. Fultz, “Irreversible Capacities of Graphite in Low Temperature Electrolytes for Lithium-Ion Batteries”, J. Electrochem. Soc., 146 (1999) 3963-3969.

8. A. Hightower, C. C. Ahn, B. Fultz, and P. Rez, "Electron Energy Loss Spectrometry on Lithiated Graphite", Applied Phys. Lett. 77 (2000) 238-240.

9. Y. Ye, C. C. Ahn, and B. Fultz, J. J. Vajo and J. Zinck, "Hydrogen Adsorption and Phase Transformations in Fullerite", Applied Phys. Lett., 77 (2000) p. 2171-2173.

10. A. Hightower, C. C. Ahn and B. Fultz “Electron Energy Loss Spectrometry on Lithiated Graphite” 2nd Conference of the International Union of Microbeam Analysis Societies, IOP Publishing; 2000: 225-226. v. Symposium 6, in press.

11. B. Fultz, C. K. Witham, and T. J. Udovic, "The Distribution of Hydrogen in $LaNi_5$ and $LaNi_{4.75}Sn_{0.25}$", in preparation.

12. B.V. Ratnakumar, R. C. Bowman, A. Hightower, C. Witham, and B. Fultz, “$LaNi_{5-x}M_x$ Alloys for Ni/Metal Hydride Electrochemical Cells,” *NASA Tech Briefs* May 1999, p. 48.

13. C. C. Ahn, Y. Ye, B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr., and B. Fultz, “Carbon as a High Capacity Solid State Storage Medium for Hydrogen”, Proc. 14th Annual Battery Conference on Applications and Devices, Long Beach, CA, January, 1999, H. A. Frank and E. T. Seo, eds., (Inst. Electrical Electronic Engs., Piscataway, NJ) IEEE 99TH8371, p. 67-71.

14. C. K. Witham, A. Hightower, B. V. Ratnakumar, R. C. Bowman, Jr., and B. Fultz , “$LaNi_{5-x}M_x$ Alloys in Rechargeable Batteries: Factors affecting Cycle Lifetimes”, Proc. 14th Annual Battery Conference on Applications and Devices, Long Beach, CA, January, 1999, H. A. Frank and E. T. Seo, eds., (Inst. Electrical Electronic Engs., Piscataway, NJ) IEEE 99TH8371, p. 61-65.

15. A. Hightower, J. Graetz, C. C. Ahn, B. Fultz and P. Rez, "The Valence of Li in Graphite", submitted to the Proceedings of the Electrochemical Society Annual Meeting, Phoenix, 2000.

5. Graduate Students supported under this grant

Olivier Delaire, Materials Science, Ph.D. expected: 2004

Jason Graetz, Materials Science, Ph.D. expected: 2002

Adrian Hightower, Ph.D. in Materials Science, California Institute of Technology, July 14, 2000.

Yun Ye, Ph.D. in Materials Science, California Institute of Technology, August 8, 2000.

Other personnel supported by this grant in 2000 have been:

Prof. Brent Fultz, Professor of Materials Science, Caltech

Dr. Heike Gabrisch, Postdoctoral Scholar, Caltech

Dr. Rachid Yazami, Visiting Associate in Materials Science, Caltech

6. Funds

Our bookkeeping shows that there will be no carryover of funds into the next year of the grant.