diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application
www.diffusion-fundamentals.org, ISSN 1862-4138; © 2005-2010

X-Ray Absorption Spectroscopy Measurements on Nanocrystalline Materials

Alan V. Chadwick, Shelley L. P. Savin*
Functional Materials Group, School of Physical Sciences, University of Kent
Canterbury, Kent CT2 7NH, UK

E-Mail: a.v.chadwick@kent.ac.uk

Presented at the Bunsen Colloquium: Spectroscopic Methods in Solid State Diffusion and Reactions September 24th – 25th, 2009, Leibniz University Hannover, Germany

X-ray absorption spectroscopy, *XAS*, is now a well established structural technique that is performed at synchrotron radiation sources. The basic principles have been covered in several books [1-3] and there have been reviews covering specific applications such as biology [4,5], catalysis [6,7], coordination chemistry [8,9] and environmental applications [10]. The main objective of this contribution is to demonstrate the unique information that the technique can provide in the materials chemistry of nanocrystalline systems. In order to attain this objective we use as case studies recent XAS experiments that have been performed on nanocrystalline oxides that are of interest in battery, fuel cell and electrochromic film applications. An additional objective is to give some insight into recent developments in the experimental techniques that can be expected to be in general use within the next few years.

We demonstrate the various applications of XAS by reference to the following systems:

1. Nanocrystalline zirconia [11] and lithium niobate [12,13] and mesoporous oxides [14] to probe microstructure.
2. Cation doped nanoceramic anatase [15-17] to locate dopant sites in crystals.
3. Nanocrystalline transition metal oxide electrodes in lithium batteries [18-20] to probe the redox reactions during charge/discharge and as examples of *in situ* experiments.
4. Delafossite materials [21] to demonstrate the applications to thin films.

The measurements on the above systems were made using conventional techniques using normal scanning modes. Thus the experiments would typically require scans of 30-60 minutes and the area probed by the beam is the order of a few square mm. The advent of more intense beams available at the new generation of synchrotrons has opened up novel developments that increase the speed of data collection and reduce the area of the probe. The final section of this contribution briefly considers time resolved XAS experiments using quick-scanning XAS [22,23] and energy dispersive XAS [24] which reduce data collection times to seconds and milliseconds, respectively, and microfocus experiments where the beam size is around 1 square micron [25]. These new developments mean that in the future experiments can be undertaken not only under *in situ* but under *in operandum* conditions. Thus fuel cells and batteries can be studied under real operating conditions.

References

[1] C. D. Garner, in: C. R. A. Catlow, G. N. Greaves, X-ray absorption spectroscopy of biological molecules, Blackie, Glasgow, 1990, p. 268.
[2] D. C. Koningsberger, R. Prins (Eds.), X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, Wiley, New York, 1988.
[3] B. K. Teo, EXAFS: Basic Principles and Data Analysis, Springer, New York, 1986.
[4] J. E. Penner-Hahn, Coord. Chem. Reviews 249 (2005) 161.
[5] C. D. Garner, Advances in Inorganic Chemistry 36 (1991) 303.
[6] B. S. Clausen, H. Topsoe, R. Frahm, Advances in Catalysis 42 (1998) 315.
[7] M. A. Newton, A. J. Dent, J. Evans, Chem. Soc. Reviews 31 (2002) 83.
[8] E. I. Solomona, B. Hedman, K. O. Hodgson, A. Dey, R. K. Szilagyi, Coord. Chem. Reviews 249 (2005) 97.
[9] J. E. Penner-Hahn, Coord. Chem. Reviews 190–192 (1999) 1101.
[10] A. Manceau, M. A. Marcus, N. Tamura, Applications of synchrotron radiation in low-temperature geochemistry and environmental sciences, Reviews in Mineralogy & Geochemistry 49 (2002) 341.
[11] G. E. Rush, A. V. Chadwick, I. Kosacki, H. U. Anderson, J. Phys. Chem. B 104 (2000) 9597.
[12] A. V. Chadwick, M. J. Pooley, S. L. P. Savin, Phys. Stat. Sol. (c) 2 (2005) 302.
[13] P. Heitjans, M. Masoud, A. Feldhoff, M. Wilkening, Faraday Discuss. 134 (2006) 67.
[14] F. Jiao, J-C. Jumas, M. Womes, A. V. Chadwick, A. Harrison, P. G. Bruce, JACS 128 (2006) 12905.
[15] R. Bouchet, A. Weibel, P. Knauth, G. Mountjoy, A. V. Chadwick, Chem. Mater. 15 (2003) 4996.
[16] P. E. Lippens, A. V. Chadwick, A. Weibel, R. Bouchet, P. Knauth, J. Phys. Chem. C 112 (2008) 43.
[17] P. Knauth, A. V. Chadwick, P. E. Lippens, G. Auer, ChemPhysChem. 10 (2009) 1238.
[18] A. V. Chadwick, S. L. P. Savin, S. G. Fiddy, R. Alcantara, D. Fernandez Lisbona, P. Lavela, G. F. Ortiz, J. L. Tirado, J. Phys. Chem. C 111 (2007) 4636.
[19] M. J. Aragon, B. Leon, C. P. Vicente, J. L. Tirado, A. V. Chadwick, A. Berko, S-Y. Beh, Chem. Mater. 21 (2009) 1834.
[20] U. Lafont, C. Locati, W. J. H. Borghols, A. Łasinska, J. Dygas, A. V. Chadwick, E. M. Kelder, J. Power Sources 189 (2009) 179.
[21] C. Yaicle, A. Blacklocks, A. V. Chadwick, J. Perrière. A. Rougier, Appl. Surf. Sci. 254 (2007) 1343.
[22] R. Frahm, Nucl. Instrum. Methods. Phys. Res. A 270 (1988) 578.
[23] L.M. Murphy, B.R. Dobson, M. Neu, C.A. Ramsdale, R.W. Strange, S.S. Hasnain, J. Synchrotron. Radiat. 2 (1995) 64.
[24] A. J. Dent, Topics in Catalysis 18 (2002) 22.
[25] A. M. Flank, G. Cauchon, P. Lagarde, S. Bac, M. Janousch, R. Wetter, J.-M. Dubuisson, M. Idir, F. Langlois, T. Moreno, D. Vantelon, Nucl. Instrum. Methods. Phys. Res. B 246 (2006) 269.