

In Situ X-Ray Spectroscopy and Imaging of Battery Materials

by Paul Shearing, Yan Wu, Stephen J. Harris, and Nigel Brandon

Lithium ion batteries have been successful in the portable electronics market. However, the demands for higher performance lithium ion batteries for electric vehicle (EV) and hybrid electric vehicle (HEV) applications have increased significantly over the past decade. To realize a wide usage of lithium ion batteries for EV and HEV, further improvement of energy density, power capability, calendar-life performance, safety, as well as a reduction in the cost of lithium ion batteries are necessary. Researchers around the globe are actively carrying out studies to address those challenges. The present review discusses the application of X-ray absorption spectroscopy and X-ray tomography as powerful techniques for probing the electrode microstructure and the atomic structure of electrode material.

X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) measures the energy dependence of the X-ray absorption coefficient at and above the absorption edge of a selected element. The main advantages of XAS are: it is element specific; it is sensitive to dilute elements (to 10-100 particles per mole); it requires relatively short times to collect experimental spectra (from miniseconds to tens of minutes) with the use of synchrotron radiation; it requires small sample volumes for analysis; and, since XAS probes short range order, it can be used to study amorphous materials and small particles.¹ Another important advantage of XAS is that both the probe and the signal are penetrating x-rays, so it permits *in situ* studies of electrode material in an electrochemical cell.

In situ X-ray absorption spectroscopy (XAS)—including the two complimentary parts, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)—has been extensively used to study the electronic and local structure of electrode materials for lithium ion batteries.²⁻⁷ The XANES portion of the spectrum at different states of charge provides useful quantitative or qualitative information about the change of oxidation state of chemical species, their site symmetries, and covalent bond strengths. EXAFS specifically probes short range order and yields coordination numbers, bond distances, and chemical identity of nearest neighbors.⁸ Overall, XAS studies provide valuable information about electrochemical reaction mechanisms and degradation mechanisms of

electrode materials during continuous cycling. The XAS results, together with the electrochemical data and other characterization information, provide deep understanding of the electrochemical reaction mechanisms and guidance on material design for lithium ion batteries.

Understanding of the redox chemistry and changes in structure during cycling is critical to design new cathode materials with superior properties for lithium ion batteries. Yoon et al.⁹ studied the charge compensation mechanism of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material, which shows higher energy density and better safety than LiCoO_2 . The metal K edge XANES and EXAFS results show that the major charge compensation at the metal site during charging is achieved by the oxidation of Ni^{2+} ions, while the manganese ions and the cobalt ions remain mostly unchanged in the Mn^{4+} and Co^{3+} state. Metal L-edge XAS results show that Ni ions at the surface are oxidized to Ni^{3+} during charge, whereas Ni ions in the bulk are further oxidized to Ni^{4+} during charge. In addition, from O K-edge XAS results, it is concluded that a large portion of the charge compensation during charging is achieved in the oxygen site due to presence of Co in the material, which is caused by the overlap of Co^{3+} : $3d\ t_{2g}$ band with the O^{2-} : $2p$ band.

LiFePO_4 is another promising candidate for cathode material due to its low cost and excellent safety characteristics. The P K-edge XAS was studied to investigate the electronic structure of the delithiated $\text{Li}_{1-x}\text{FePO}_4$ material, and it shows that the electrochemical delithiation of $\text{Li}_{1-x}\text{FePO}_4$ results in the hybridization of P 3p states with the Fe 3d states.¹⁰ The *in situ* XANES spectra at the Fe K-edge during charge give useful information as how the LiFePO_4 is changing gradually to FePO_4 phase. Detailed analysis on the main edge and the pre-edge characteristics show that Fe^{3+} and Fe^{2+} in $\text{Li}_{1-x}\text{FePO}_4$ during charging are in octahedral coordination of the oxygen atoms and the structural rearrangement on lithium extraction in $\text{Li}_{1-x}\text{FePO}_4$ is small which leads to the great stability of LiFePO_4 material during cycling.^{11,12}

Recently, there has been an immense interest in the Li-rich solid solution layered cathode $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Mn}, \text{or Co}$) which exhibits a capacity of 250 mAh/g. These materials have been extensively investigated to understand their complicated crystal structure and the origin of their high capacity, which exceeds their theoretical capacity based on conventional chemical concepts.¹³⁻¹⁶ When charged

above 4.5 V, a long irreversible plateau appears in the voltage profile. From neutron diffraction analysis and *in situ* differential electrochemical mass spectrometry, Armstrong et al. suggested that lithium extraction above 4.5 V is accompanied by a loss of oxygen.¹⁷ The commonly accepted charge-discharge mechanism of this cathode material is the irreversible loss of oxygen from the lattice during the first charge plus lowering of the oxidation state of the transition metal ions at the end of first discharge compared to the oxidation state value in the initial material.

X-ray absorption spectroscopy including XANES and EXAFS measurements has been applied to study the change of oxidation state of Ni, Co, and Mn of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ material during charge-discharge.¹⁸⁻²¹ It is found that Ni, Co, and Mn exist as 2+, 3+, and 4+ in the pristine material. During charging and discharging, Ni and Co get oxidized and reduced reversibly; however, it is difficult to determine the change of valence state for the Mn ion due to the complicated energy shift of the Mn K-edge absorption. So instead, Mn K pre-edge was used to examine the change in the valence state of Mn, as shown in Fig. 1, and it was determined that Mn^{4+} gets reduced to $\text{Mn}^{3.6+}$ after 1st discharge.²¹ However, based on the charge compensation of Mn, Co, and Ni, the reversible capacity of this cathode material is only 199 mAh/g, much lower than the 266 mAh/g observed experimentally. Studies on additional charge compensation using XAS will be necessary to fully understand the high capacity mechanism of this material.

As discussed previously, oxygen involvement in the redox reaction is very important to understand the electrochemical reaction and degradation mechanism. The XAS study for the cathode materials of lithium ion batteries has concentrated on the absorption peak features of the transition metal K-edge spectrum. However, the metal K-edge XAS could not give any direct information for participation of oxygen in the charge compensation process. Soft XAS (200-1000 eV), using synchrotron radiation, has been applied to investigate the electronic structure of oxygen and fluorine in the electrode materials for lithium ion batteries.²²⁻²⁶ However, *in situ* soft XAS studies of oxygen K edge for lithium ion batteries have been limited because of the high vacuum condition required for the measurements. Also, complicated cell and electrode components, including organic binders and liquid electrolytes,

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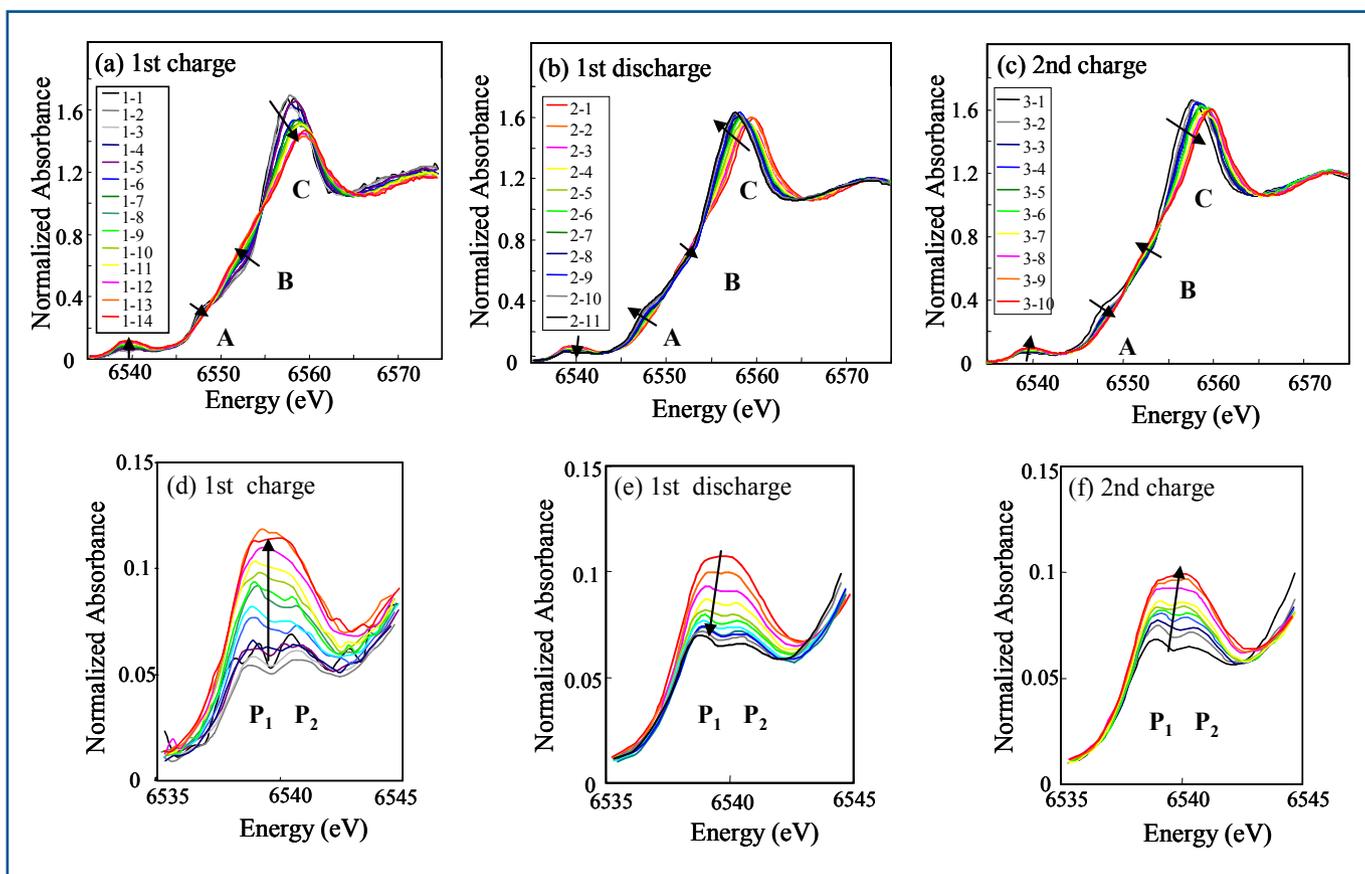


FIG. 1. Normalized XANES spectra of the Mn K edge and Mn K pre-edge of $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ during the initial charge-discharge.²¹

are required. Thus novel design of the electrode and cell is required to get high quality data for *in situ* soft XAS measurement.

X-Ray Tomography

Reactions in lithium ion batteries are supported by porous electrode microstructures. The electrode comprises a number of phases, the active material, conductive additive, binder, and solid electrolyte interphase (SEI) layer. It is important to understand the complementary role of each of these phases in battery operation, as each will contribute to overall cell performance. These porous electrode microstructures are expected to support a range of physical phenomenon and therefore, in common, with all functional materials there is a direct link between the electrode microstructure and its performance. However, in spite of the clear importance of lithium ion battery electrode microstructure, we have only a limited understanding of what these structures are, and how they change during processing, operation and failure. For example, in operation, graphite anodes are known to expand as Li becomes intercalated during cell discharge with volume changes of ca. 10%. For alloying type electrodes, such as Sn or Si compounds, volume changes

of up to 400% have been observed.²⁷ Microstructural evolution occurs due to volume changes as a function of the state of lithiation—the mechanical stresses generated by these evolution processes can also drive microstructural degradation processes over longer time scales. As well as particle shape change, additional problems such as Ostwald ripening and sintering are also associated with alloying electrodes,²⁸ indeed the problems in managing charge cycling in these novel high capacity materials has driven development of a number of proprietary nano-wire technologies.

Over the past 20 years, a large number of microstructural investigations of lithium ion battery electrodes have been performed using a suite of microscopy tools such as optical microscopy,^{29,30} scanning electron microscopy,³¹ TEM,³² and AFM,³³⁻³⁵ alongside techniques such as TOF-SIMS³⁶ and NMR.³⁷ Techniques including TEM, AFM, and optical microscopy have also been used to explore microstructural evolution processes associated with charge cycling in a variety of battery materials. The wealth and quality of these papers illustrates the success of these conventional 2D tools. However some phenomena, such as percolation, are inherently three-dimensional and as such stereological interpretations from 2D data sets can prove ambiguous.³⁸

Recent advances in tomographic techniques have enabled three-dimensional microstructural characterization of a wide range of materials with unprecedented resolution. A range of techniques of varying resolution are now available; these include: atom probe tomography, electron tomography, X-ray computed tomography (CT), and focused ion beam (FIB) tomography. Two recent reviews of the state-of-the-art in nano-tomography provide a thorough introduction to FIB and electron techniques,^{39,40} Withers⁴¹ provides a summary of the latest developments in X-ray techniques and Miller and Forbes⁴² review the status of atom probe tomography.

Here we focus on developments in X-ray computed tomography and explore its application to the field of battery materials engineering, but also consider relevant studies utilizing other techniques including neutron tomography and focused ion beams.

The choice of tomography technique is primarily dependent on a balance of the sample volume that needs to be characterized, and the resolution required to quantify relevant feature sizes. Additional considerations involve the physical and chemical nature of the sample under consideration; for example, its X-ray attenuation coefficient or the rate of ion beam milling. The choice of tomography technique is therefore very

application specific; often the use of more than one technique can provide complementary information and help to validate results.⁴³

The resolution of a conventional X-ray system is determined by the X-ray spot size; this is a function of the X-ray source and the working distance between the sample and the source. This in turn determines the X-ray field-of-view (FOV) and magnification.

In geometrically magnified systems, the resolution is ultimately a function of the sample size, as this dictates the source-sample working distance. In conventional lab systems the resolution is limited to ca. 3 microns. The increasing availability of “nano-focus” X-ray sources is, however, driving down the spatial resolution achievable, with manufacturers reporting resolved features of ca. 700 nm.⁴⁴ SEM hosted X-ray CT scanners utilize the electron beam in a conventional electron microscope to generate X-rays from a range of metal targets. The energy, flux, and resolution of the system are dependent on the e-beam and target used. In synchrotron environments, the high flux and mono-chromaticity, coupled with a highly parallel beam, facilitate high-resolution studies of relatively large samples, without the penalties incurred in cone beam systems with geometrical magnification. Further, with implementation of X-ray optics, for example Fresnel zone plates, synchrotron based CT can routinely achieve sub-100 nm resolution with high throughput.⁴⁵ A more detailed description of the physics of X-ray optics is provided by Banhart et al.⁴⁶ Laboratory lens based systems can focus the source and transmitted beam thereby improving the resolution that can be achieved in conventional lab machines. While the flux in laboratory systems is orders of magnitude below the synchrotron beam lines, comparable spatial resolution has been demonstrated, albeit with longer scan times.

The ability to characterize battery electrode microstructures with spatial resolution spanning more than an order of magnitude provides the opportunity to explore these highly complex materials at a length scale relevant to the physical phenomena occurring within them. The development of these tomography platforms has recently allowed the study of battery microstructures in three dimensions—enabling for the first time, direct quantification of particle and electrode geometries with opportunities to explore the effects of manufacture, aging, and failure, and to explore the relationship between microstructure and performance.

The first high-resolution tomographic study of lithium ion battery electrodes was published by Shearing et al. in 2010⁴⁷ as shown in Fig. 2. The study demonstrated the potential to use tomography to study carbon based

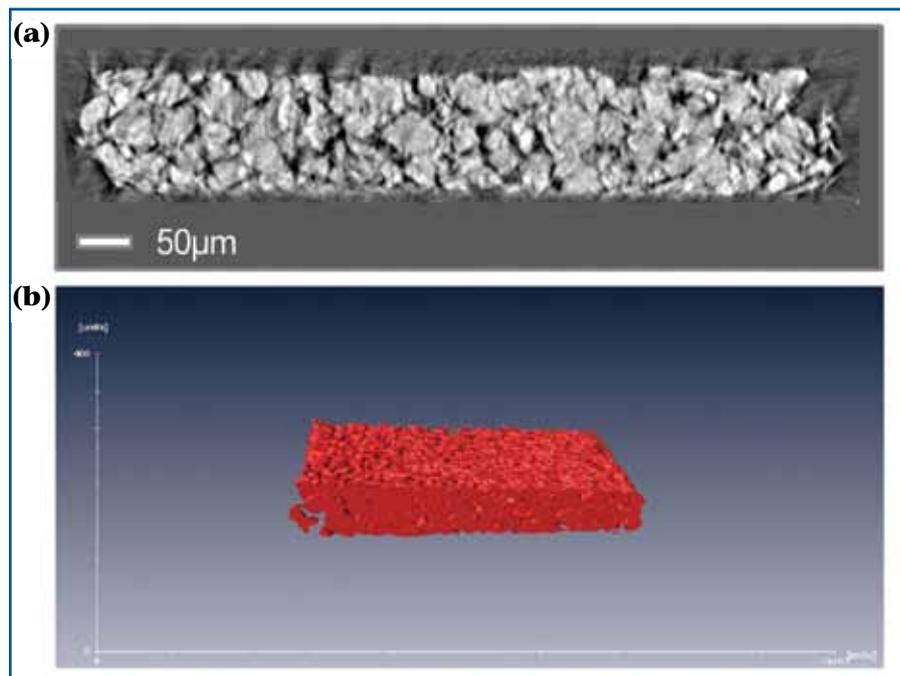


Fig. 2. (a) Individual slice from the tomography sequence. (b) Rendering of 300 individual tomography slices (dimensions 43×348×144 μm).

materials at length scales appropriate to Li battery electrode studies.

Focused ion beams (FIBs) have also been successfully employed in the study of lithium ion battery microstructures—combination of the nanoscale milling power of ion beams with conventional electron microscopy provides the opportunity to sequentially mill and image a sample, yielding a sequence of 2D images that can be effectively recombined in 3D space. Because of the characteristically smaller particle size and the problems inherent in ion beam milling graphite, the use of FIB tomography techniques show more promise for studies of lithium ion battery cathode microstructures.⁴⁷ Focused ion beam techniques have been successfully utilized to explore cathode particle morphologies for LiCoO_2 ⁴⁸ and $\text{Li}(\text{Co}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3})\text{O}_2$ ⁴⁹ systems. Reconstructions of individual electrode particles reveal highly irregular morphologies and internal cracking which will affect Li transport and stress distributions. Ender et al.⁵⁰ have also used FIB techniques to explore the distribution of active particles and conductive carbon in the composite LiFePO_4 system.

Because of the broad range of physical phenomena occurring in lithium ion batteries, it is desirable to conduct tomography at multiple length scales—including studies at the cell and pack level. At the pack level, Yufit et al.⁵¹ have recently utilized conventional laboratory CT to explore changes in the architecture of a lithium-polymer cell after catastrophic failure. More recently, studies of Li coin cells have resolved the microstructural detail of constituent electrodes, without the requirement for

cell deconstruction—highlighting the potential to explore changes in the cell microstructure at various stages of cell lifetime.⁵²

With improved access to high resolution tomography data it is possible to effectively combine real-life microstructural data with relevant simulations—this has been especially productive in the field of Solid Oxide Fuel Cells, where this combined modelling and experimental approach has given insight into the performance-microstructure relationship. While in its infancy for lithium ion battery electrodes, there is, nonetheless significant interest and promise in this area. Recently Kehrwald et al. successfully utilized a 3D reconstruction of a graphite anode as the basis for a transport simulation.⁵³ In this study, diffusion of an arbitrary diffusing species was modelled in the “real-life” electrode geometry as a conduit to evaluation of the Bruggeman relationship. Ender et al.²⁶ also utilize their FIB derived tomography data as the basis for a finite element transport simulation—in doing so the authors effectively analyzed and compared tortuosity as defined by geometry, transport limitation, and the Bruggemann relationship. These papers present an important first step in the adoption of realistic geometries for transport simulations, as well as a means to link performance and microstructure for working lithium ion battery electrodes.

Tomography techniques provide access to detailed microstructural data in three dimensions. Extending these techniques to explore temporal

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changes in functional material microstructures gives rise to the notion of “4-dimensional” tomography to study microstructural evolution processes in the time domain.

Destructive techniques, such as FIB tomography, are inherently limited in their ability to capture the dynamics of microstructural evolution as the statistical differences in material microstructure can often cloud the interpretation of microstructural change (Shearing thesis). Utilizing the uniquely non-destructive X-ray methodologies with spatial resolution relevant to these materials, it is possible to observe microstructural evolution processes *in situ*. Chao et al.⁵⁴ have utilized transmission X-ray microscopy to study *in situ* lithiation of Sn particles. The expansion behavior is observed, the rate of which is found to be inversely proportional to the inverse square of the particle diameter. Furthermore, upon cycling the Sn particles, evolution of a porous microstructure is observed. While this study is only conducted in 2D, with improvements to the experimental setup, 3D studies should be possible. In alkaline battery chemistries, Haibel et al.⁵⁵ have demonstrated the use of synchrotron X-ray CT to study a LR61 (AAAA) Varta HighEnergy Cell, successfully identifying changes in the zinc microstructure during operation.

Kardjilov et al.⁵⁶ utilize neutron tomography to study Li coin cells at various stages in the discharge process, the heavily penetrating neutrons provide a means of mapping microstructural change during operation albeit at limited resolution. The neutron mass attenuation coefficient for Li is favorable for isolation of Li distribution—this is not currently possible using X-ray techniques because of the extremely limited attenuation of X-rays by lithium; however, progress in the study of ultra low-Z materials using phase contrast X-ray imaging may point to opportunities for study of lithium dendrites previously only achievable by neutron and NMR techniques.

With continuing developments in the temporal and spatial resolution of X-ray techniques combined with phase contrast and XANES tools, the battery community is increasingly equipped to explore the effects of microstructure on battery performance. Combination with relevant simulation provides a means of isolating microscopic contributions to conventional measures of macroscopic performance and 4D techniques will enable studies of aging and failure of these devices; and ultimately, these techniques will provide valuable information to inform the design of future generations of high performance battery materials.

Conclusion

The results and discussion above show that X-ray absorption spectroscopy and tomography are important tools in determining the electronic structure and microstructure of the electrode materials. With further development of these *in situ* measurements in combination with other characterization techniques, we foresee great advance in material and electrode design of lithium ion batteries.

About the Authors

PAUL SHEARING is a chemical engineer with research interests in electrochemical devices, particularly fuel cells and Li-ion batteries. Dr. Shearing's research explores the relationship between microstructure and performance for these functional materials, using X-ray and electron microscopy techniques in tandem with advanced modeling tools. He is a lecturer in Chemical Engineering at University College London and may be reached at p.shearing@ucl.ac.uk.

YAN WU is a research scientist at General Motors R&D Center. She is active in research and development of high capacity cathode material for lithium ion batteries. She may be reached at yan.wu@gm.com.

STEPHEN J. HARRIS received a BS degree in chemistry from UCLA in 1971 and a PhD degree in physical chemistry from Harvard University in 1975. After a two-year Miller Institute postdoctoral fellowship at UC Berkeley, he began working in the Physical Chemistry Department at General Motors Research Labs in 1977. He switched to the Chemistry Department at Ford Research Labs from 1998 until 2007, after which he returned to General Motors, where he is currently a Technical Fellow in the Electrochemical Energy Research Department. He will be a Miller Institute Visiting Professor at UC Berkeley in 2012. During his more than 30-year career at GM and Ford, Steve has worked in a wide range of different fields, including: laser diagnostics of combustion and laser-induced chemistry; soot formation, aerosol dynamics, and the chemistry of rich combustion systems; modeling and experimental chemical vapor deposition of diamond and boron-containing films; development of tribological coatings; contact mechanics modeling and prediction of fatigue lifetimes; solid oxide fuel cell chemistry; microscopic basis for ductility and fracture in cast aluminum; and microscopic bases for transport and degradation in lithium-ion batteries. He may be reached at harris.stevharris@gmail.com.

NIGEL BRANDON is Director of the Energy Futures Lab at Imperial College London. His research interests focus on electrochemical power sources and their role in low carbon energy systems. He heads the UK SuperGen fuel cell consortium, and was a founder of fuel cell developer Ceres Power in 2001. He may be reached at n.brandon@imperial.ac.uk.

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