



Editors' Choice—Review—John Goodenough's Impact on Electrochemistry in Oxford's Inorganic Chemistry Laboratory

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This paper covers the period following the appointment of John Goodenough to the Chair of Inorganic Chemistry at Oxford University and the development of the electrochemistry group in the Inorganic Chemistry Laboratory under his leadership. The paper details the studies he initiated into semiconductor electrochemistry and photoelectrochemistry, electrocatalysis, fuel-cell development and battery research, and the way in which these studies complemented each other. A brief account of some of the later developments in electrochemical research at Oxford is given, showing how these developments grew out of Goodenough's earlier ideas and ambitions.

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Manuscript received October 12, 2021. Published February 1, 2022. *This paper is part of the JES/JSS Joint Focus Issue In Honor of John Goodenough: A Centenarian Milestone.*

Arrival and Starting Up

The electors' choice of John Goodenough in 1975 as the new Professor of Inorganic Chemistry at Oxford was greeted with what might be euphemistically termed surprise within the discipline in the UK. The chair was a recent creation: its first occupant was a highly regarded solid-state and surface chemist, JS Anderson, who had been head of the National Chemical Laboratory at Teddington before his appointment to the Oxford chair, and whose reputation had been cemented by his work in non-stoichiometric solid-state chemistry, and in field-emission studies on solid-surface reactions. He was also the co-author of a highly successful textbook "Modern Aspects of Inorganic Chemistry" with HJ Emeléus.¹

The electors determined to appoint another solid-state scientist to the Oxford Chair, perhaps to ensure balance within the UK community of inorganic chemistry. The choice of Goodenough was both extraordinary and inspired, bringing to the UK an expertise in electronic and structural solid-state science that transcended conventional subject boundaries^{2,3} and was to have a significant impact on electrochemical thinking, particularly as the latter discipline extended its thinking to include novel metals and semiconducting electrodes.

Goodenough arrived to a set of first-floor laboratories that had been cleared to accommodate him, and a starter grant that would allow him the purchase of a reasonable amount of basic equipment to initiate studies in both solid-state chemistry and electrochemistry/photoelectrochemistry. He was also given two junior demonstrator posts to enable him to start experimental studies in these areas: one was Dr Philip Wiseman, a very able solid-state chemist, and the other was myself. Actually I had had limited experience in electrochemistry up to that point: my main interests had been in spectroscopy and electronic structure, but I had been tutored by John Albery, at that time the resident electrochemist in the Physical Chemistry Laboratory at Oxford, for whom I had written undergraduate essays on the hydrodynamic theories of Levich, and on the application of quantum mechanics to electron transfer in electrochemical reactions. Goodenough made it clear that he was not looking for a conventional electrochemist, but for someone with an extensive background in optical and theoretical science, and I was very happy to join him on that basis, but I would want immediately to acknowledge the enormous help that Albery gave to us in setting up an experimental electrochemical group in the Inorganic Chemistry Laboratory. The collaboration between Albery, shortly thereafter to depart to Imperial College, and the Goodenough group

very substantially shortened the time between the latter's arrival and our first papers, and lasted for a decade.

The Challenge Put Down by John Goodenough

On my appointment at the very end of 1976, John Goodenough led me through his thinking in terms of the major problems, as he saw them, of the future of energy generation on the global scale. It was evident to him that sooner or later the world would exhaust the fossil fuel supplies that had been laid down in earlier geological times, and that as supplies tightened, prices would rise and energy would become a commodity over which wars would be fought. The only sensible source of energy for the future was solar energy, but this was both diurnally and seasonally out of phase with our requirements. We need heat and light in the winter nights, when direct solar energy is unavailable.

The solar energy harvested, therefore, during the Summer days would need to be stored in some form for those winter evenings, and there were two possible routes: the first was to convert the Sun's energy into stable high-energy-content chemicals that could be safely stored for long periods; the second route was the development of batteries of sufficient stability to allow energy storage on at least an annual timescale, and with sufficient energy and power density to drive vehicles.

With regard to chemical storage, the obvious vector was hydrogen: this can be generated from aqueous electrolytes and either used directly in fuel cells to regenerate electricity or converted to some liquid (and more easily transportable) fuel, such as methanol. The generation of hydrogen could be by electrolysis of aqueous electrolytes using photovoltaic devices, but Goodenough's thinking had been stimulated by a paper from Fujishima and Honda⁴ in which TiO₂, lightly *n*-doped, had been shown under illumination and positive bias to evolve oxygen. If this could be coupled to an efficient hydrogen-evolution electrocatalyst it would allow a self-generating system to be developed, which evolved oxygen at the semiconducting anode and hydrogen at the counter-electrode. Whilst the electronic structure of TiO₂ was such that its flatband potential was too positive to use without a biased cathode, it had already been shown that replacement of the TiO₂ electrode with SrTiO₃ lowered the flatband potential by raising the energy of the antibonding Ti:3d band and allowed such a device to be built.⁵ Unfortunately, the *bandgap* of SrTiO₃ was too high, since the O:2p non-bonding levels were at a similar level to those in TiO₂; the first project suggested by John was to find an electrode with a similar flatband potential to SrTiO₃ but with a smaller bandgap.

The second project was to develop an improved lithium-ion battery. John was convinced that lithium-based batteries would offer good prospects of reversibility owing to the smallness of the lithium

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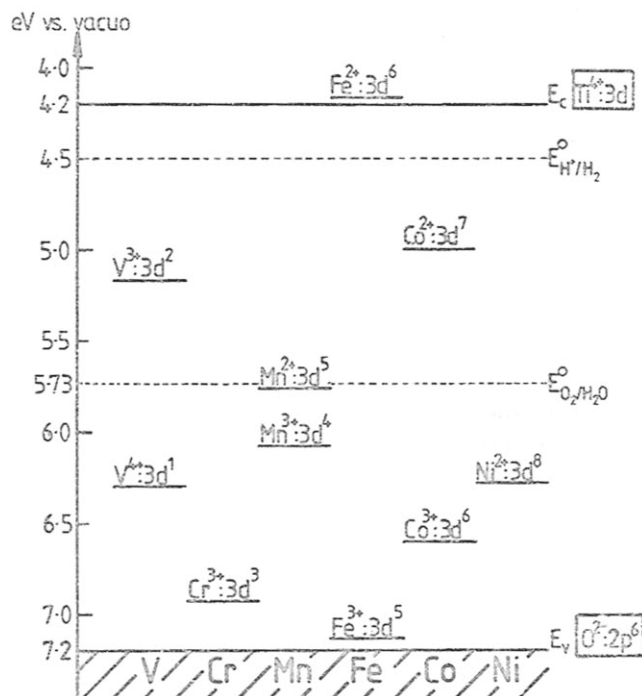


Figure 1. Energy levels of various first-row metal ions doped into TiO_2 .¹²

ion, which should make it mobile in at least some lithium compounds, and its low atomic weight and high negative electrode potential would allow very substantial improvements in both energy and power density, as compared to more conventional metal-ion based batteries. Whittingham⁶ had written an important article, in the year of John's arrival, on intercalation chemistry and lithium-battery design, though his own choice of intercalate, TiS_2 , had not proved very stable nor, as John saw, would a sulfide have the right energy levels to sustain the high voltage which the batteries might theoretically attain.⁷ John's second challenge was therefore to devise oxide-based intercalation compounds that could be used with appropriate counter-electrodes in a lithium battery.

John recognised that solar photovoltaic light harvesting coupled with water electrolysis was an attractive alternative to the one-stop photoelectrochemical devices he was interested in, and he also recognised that the subsequent conversion of the hydrogen back into electrical power would be potentially far more efficient if better performance fuel cells could be constructed. The main limitation in the efficiency of both aqueous electrolysis and fuel cell performance was well known to be the poor electrode kinetics of the oxygen evolution and reduction reactions.⁸ Multi-electron electrochemical reactions are notoriously difficult to catalyse effectively: one or other of the intermediates may be either highly unstable or bond so strongly to the surface that subsequent reaction steps are blocked. These were very early days in terms of the more detailed theoretical understanding of the electrode/electrolyte interface now emerging, but John felt it would be worthwhile exploring metallic oxides as catalysts, particularly those with potentially interesting surface structures.

Related to this was the developing interest that John had in the problems of hydrogen gas as a main energy vector: even in developed nations, where gas pipelines had been laid down at earlier times to distribute coal gas, there are not insignificant difficulties in converting these pipes for use with hydrogen. The gas would also need to be stored remotely either at high pressures or in liquefied form, both of which carried considerable risk. It would be much better from this point of view if the main energy vector were a liquid, such as methanol, which could be synthesised from CO_2 and H_2 . In principle, the methanol could be combusted in a modified

internal combustion engine, but it was evident that much better efficiencies could be obtained, at least in principle, using an electrochemical fuel cell, either directly oxidising the methanol at a suitable anode or reforming the methanol to hydrogen before using a more conventional fuel cell. John was interested in the direct electro-oxidation of methanol, and again saw metallic oxides as potential electro-catalysts.⁸

It is clear from the above brief summary that John Goodenough had developed a very full programme of work before arriving in Oxford: the combination of solid-state chemistry and electrochemistry in his hands would be a very powerful tool and we set about working in each of the areas above, moving on as our knowledge grew.

The Work in Oxford on the Goodenough Challenges

Semiconductor electrochemical studies.—Work on the *n*-type semiconductors began as soon as the equipment was ready. To carry out meaningful work on the electrochemistry of semiconductors, we first needed to master the literature.^{9,10} We swiftly found that electron affinity of the perovskite titanates could be adjusted by replacement of the Ti by Zr but this gave compounds of the type $\text{SrTi}_{1-x}\text{Zr}_x\text{O}_3$ that had very large bandgaps, though subsequently we found that these did have interesting surface electrochemistry,¹¹ which we thought was due to facilitated peroxide formation. It was clear that we would need to insert an electronic band between Ti:3d and O:2p, and fortuitously Dr Mizushima had come to work with John on data he had obtained from photoconductivity and e.s.r., data on the energies of metal ions embedded in TiO_2 . This data is summarised in Fig. 1.

Using these data, it appeared that only $\text{Cr}^{3+}: 3d^3$, $\text{Mn}^{2+}: 3d^5$ and $\text{Ni}^{3+}: 3d^8$ were likely candidates. It was expected that complications might arise from substituting on the Ti(IV) sites,¹³ theory suggests that at moderate positive bias, the mobilities both of holes (in the d-band of the substituent metal) and electrons (in the T: 3d band) might be adversely affected, but Dr Guy Campet, working with the group, found that $\text{SrTi}_{1-x}\text{Cr}_x\text{O}_{3-y}$ did show an interesting photo-response in the visible at high bias potentials.¹⁴ Careful investigation, however, revealed that at lower potentials, the holes arriving at the surface converted Cr(III) to Cr(IV) but that this was unable to oxidize water at lower bias potentials. A similar conclusion was reached for $\text{NaCeTi}_2\text{O}_6$, where our attempts to exploit the $\text{Ce}^{3+}: f^1$ band led to the same problems.¹⁵ Placing the Ti and M ions on separate sub-lattices was also tried using the ilmenite structure, but here the oscillator strength for the $\text{M} \rightarrow \text{Ti}$ transition was poor in the case of MnTiO_3 , and again surface kinetics for O_2 evolution were bedevilled with surface polaron formation. In the end more than 20 substituents were tried; we learned a great deal about hole transport and surface electron-transfer kinetics from these studies but we did not succeed in finding a compound that could act in the way we sought.

It became clear to us, working with *n*-type semiconductors, that we could relax the extremely demanding conditions on the photanode by coupling it with a photocathode. This entailed a new project on *p*-type semiconductors, carried through by a very able D.Phil. student, Dr Martin Dare-Edwards.¹⁵ Initially, we concentrated on (III/V) semiconductors with bandgaps in the visible-light region. Subsequently, we hoped to couple these materials to an appropriate oxygen-evolution catalyst, with the holes photogenerated in the cathode being passed to the anode.

To gain experience, Martin carried out a very thoroughgoing study of *p*-GaP in 0.5M H_2SO_4 .¹⁶ This material, with a bandgap of 2.2eV, gave very good agreement with expected photocurrent/voltage behavior at potentials more than about 0.6V negative of flatband potential, but as flatband was approached, the photocurrents vanished, an effect traced after considerable numerical modelling to a surface-state model, with the surface state itself being photogenerated. This came as a very unpleasant surprise, and seemed to be replicated in other III/V materials as well. In general, the poor

overall kinetics for H₂ generation raised a large question mark over the use of these materials in aqueous photoelectrolysis cells. Martin studied several other materials, including p-GaAs, p-InP and p-GaSb,¹⁵ and we also studied the possibility of fixing CO₂ with these materials, but whilst we did obtain some evidence of reduction to HCHO, we did not detect methanol and we found the stability of these semiconductors poor over long periods.

An analysis of the energetics for p-type semiconductors also revealed that coupling such a semiconductor to an O₂ evolution catalyst made severe demands on the valence-band energetics if holes deep enough in energy to oxidize water were to be formed. Only oxides appeared to have the requisite valence-band energy and p-type semiconducting oxides are not common. We carried out an intensive study of one of these: p-NiO.¹⁷ The study revealed that the now extensive instrumental capability we had built up could give a detailed picture of the surface electronic structure of this material, but it was only at photon energies above 3.5 eV that we could obtain photocurrents from the O: 2p → Ni: 3d transition. These currents were small, and it became clear that the high dopant densities needed to obtain reasonable conductivity in the oxide and the concomitant high recombination rates made this compound unattractive as a photocathode.

The only other p-type oxide investigated in depth was p-PdO, grown as a single crystal.¹⁸ Although the bandgap of this material is small (0.8 eV), this corresponds to a strongly forbidden d-d transition, with the O:2p → Pd: 4d transfer appearing at 2.2 eV. The photoresponse was poor, partly through poor bulk carrier properties and partly through very poor surface kinetics for H₂ evolution. A major competing surface process proved to be surface Pd(II) reduction.

Amongst other approaches tried was that of dye sensitisation, in which a monolayer of dye molecules is bonded to the surface of an n-type oxide semiconductor, and sub-bandgap illumination at and near the absorption maximum of the dye molecule is used to excite the molecule into a state capable of injecting an electron into the conduction band of the semiconductor. This work was carried out by another good D. Phil. student, Dr. Ray Wright, in conjunction with a colleague in the Inorganic Chemistry Laboratory, Professor Ken Seddon.¹⁹ It became very clear that the method of attachment of the dye to the oxide surface was critical, and in addition, the oxidation of water by the oxidised form of the dye chosen, Ru(bipy)₃²⁺, was much slower than hoped, leading to accumulation of charge at the surface. At potentials close to flatband, a further loss of efficiency was associated with re-reduction of the oxidised dye molecules by the capture of majority carriers within the depletion layer. For the purposes of photo-electrolysis, we therefore abandoned this approach.

New electrocatalysts.—The experience of poor kinetics for the oxygen evolution reaction led to John to pay attention to the possibility of designing better catalysts based on metallic oxides. This also would permit the development of improved fuel cells, another objective of the group. Oxygen reduction clearly depended on transport of the O₂ molecules to the electrode surface, and their capture at the surface for a sufficiently extended time to permit the 4-electron reduction needed. John speculated that this would require an oxide with controlled oxygen-site defects and with a metal ion with (ideally) several easily accessible oxidation states, so that multiple electron transfer might be possible. He suggested lead ruthenate, which had been written in the earlier literature as PbRuO₃, but which was now known to have a defect pyrochlore structure Pb₂Ru₂O_{7-y}.²⁰ This and the pyrochlore Bi₂Ru₂O₇ were known already to show promise in oxygen reduction,²¹ but we carried out a substantial study on these and other ruthenates. By varying the counter-cation in these ternary oxides, we could alter the Ru: 4d bandwidth in a systematic fashion, and we found that the narrower the bandwidth, the more well-defined the cyclic voltammogram features became—it was clear that surface polaron formation was substantially affected by the bandwidth.²²

An extensive study of the oxygen-reduction electrochemistry by a very capable D.Phil. student, Chris Naish, showed that the exchange-current densities for these materials were similar to those observed on Pt, suggesting that the kinetics for oxygen reduction depended on a similar mechanism.^{22,23} Detailed analysis of the kinetics suggested that an outer-sphere electron transfer process might be followed by a rate-determining nucleophilic attack by O₂H on surface Ru. This would account for the kinetics at low overpotential, but at higher overpotentials the Tafel slopes become very large, suggesting that the rds is the initial displacement of increasingly highly structured surface-bound water by the incoming O₂. The activity of these ruthenates is most marked in alkaline solution, and stability problems are encountered in more acidic regimes; however, even in alkaline solutions, there is evidence of slow leaching of the Pb out of the cathode.

Amongst other materials studied was platinum phthalocyanine, which grew out of an interest in the very high stability of this compound, and which we could explore with the hydrodynamic tools developed with the help of John Albery.²⁴ This proved quite active as well, and particularly so when deposited as a thin layer on activated carbon. This latter approach had been adopted by the group as a means of stabilising our electrocatalysts, with the very considerable help of Dr Ashok Shukla,²⁵ and the properties of the carbon were the subject of a careful and thoroughgoing analysis by the Oxford group.²⁶ Both the ruthenates and PtPc could be deposited using techniques developed by Dr Shukla, and gave very stable films with considerable enhancement of the clean 4-electron reduction.

John had, meanwhile, been reflecting on the difficulties of using H₂ as a vector, and had concluded that liquid methanol might prove a better bet. The electro-oxidation of methanol had been studied for many years on platinum and other noble metals,^{27,28} and it was clear to John that the problem of oxidation of methanol required both the initial adsorption of the molecule on an appropriate surface and its subsequent conversion to CO₂, a process requiring 6 electrons. The mechanism envisaged evidently required multiple steps, a supply of some form of active O from the surface and the removal of six H⁺ ions. In addition, the process would have to be carried out in acid, since in alkaline solution carbonates would form that would prove difficult to extract using normal technologies; this severely limited our options in terms of oxide-based catalysts. We had some very helpful initial conversations with the Shell methanol fuel cell group of the time,²⁹ who had developed highly active Pt/Ru anodes; it was clear that the Pt provided a useful surface for the initial adsorption process, which appeared to proceed to either ≡C–OH_{ads} or CO_{ads}, and the Ru, presumably present as hydrous RuO₂ or something similar, would then engage in a redox O-transfer reaction to form CO₂.

The initial experiments compared co-precipitated Pt/Ru either unsupported or supported on carbon,³⁰ very long-term experiments showed that the unsupported catalysts very slowly degraded, but that activity was quickly lost on the supported catalysts. These experiments suggested that the pre-treatment of the carbon support and the method of deposition of Pt were quite critical; electron microscopy and XPS were employed to get a better feel for this:³¹ a study by another able post-doctoral fellow, Brendan Kennedy, together with another very capable D.Phil. student, Simon Weeks, showed that very small Pt crystallites and carbon-black substrates seem to encourage the formation of OH_{ads}, and data suggested that Pt itself becomes partially oxidised in these samples as well as revealing the presence of an adsorbed oxidised C species thought to be formate.³²

The fact that RuO_x species can strongly catalyse methanol oxidation led John to wonder if other base-metal oxides might work: a study by Brendan revealed quite a mixed bag, with the group V metal oxides promoting the activity of Pt at all current densities, whereas others either inhibited the performance entirely or promoted only at lower potentials.³³ XPS revealed considerable detail of the mechanism, but toward the end of John's tenure, we decided we needed in situ Infra-red to make sense of the complex processes on these catalyst surfaces. We had a very gifted post-doctoral student, Paul Christensen, who, with some help from Alan Bewick at

Southampton University, was able to set up this technique and subsequently to obtain extremely helpful results.³⁴

New battery materials.—The other important string to John's bow was the development of improved batteries for energy storage. This was recognised by John very early on as essential if the use of solar power was to become widespread, and the two key aspects of the work were (a) to ensure that the Li⁺ ion could enter and leave the structure easily and (b) that the structure would be stable to the depletion or addition of Li.

The first of these strongly suggested to John that we needed to work with interstitial materials, as already suggested by Whittingham,⁶ in which the Li⁺ ion occupied layers in the solid within which they would be relatively mobile and easily extracted. John was convinced that only oxides would be able to sustain the large potentials that lithium batteries should be capable of, and given the need for structural stability, these oxides would need to possess at least one metal ion that could be oxidised to compensate for loss of Li⁺ during charging. Methods for measuring ionic mobility in solids needed to be set up and cell monitoring equipment and dry-box facilities were absolutely essential. All this was managed by Philip Wiseman, working closely with John and other colleagues, and the subsequent development of LiCoO₂³⁵ as well as other potential solid-state battery materials has been reviewed elsewhere.⁷

Later Developments

The arrival of John Goodenough coincided with the development within electrochemistry of a wide range of new techniques using spectroscopic and structural tools to investigate the nature of the electrode-electrolyte interface. We found that these could be combined very fruitfully with John's own insights into the effects of electronic and crystal structures on electrochemical behavior. The study of complex electrochemical processes has been revolutionised using infra-red and Raman spectroscopy; our studies of semiconducting electrodes revealed the need for techniques such as electro-reflectance to pinpoint the distribution of potential at the electrode-electrolyte interface; the introduction of active electrochemical films needed both in-situ techniques such as ellipsometry and ex-situ techniques such as XPS and electron scattering. Electrochemistry is now a very different discipline from that of two generations ago; it is fair to say that John's own influence on this development has been a very significant one of which he can be proud.

Acknowledgments

John and I were fortunate to attract many very able co-workers, some of whom are mentioned above. In addition, many came to work with John on solid-state non-electrochemical projects, and all made important contributions to a very lively scientific period in Oxford. I have already indicated my indebtedness to John Albery, but I would also want to thank the technical staff of the Inorganic Chemistry Laboratory in the 1970s and 1980s, and very particularly to thank Dr Peter Trelvellick whose astonishing programming and

electronic skills allowed us to develop a whole raft of advanced techniques.

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