Institution: EaStCHEM

Unit of Assessment: 8 (Chemistry)

Title of case study: New Generation Rechargeable Lithium Batteries

1. Summary of the impact (indicative maximum 100 words)

Impact: The impact reported here is on the development of new generations of lithium battery technologies, and is primarily economic, with beneficiaries ranging across all the major battery manufacturers in Asia, Europe and the Americas. Consumers and society at large have been impacted significantly through the introduction of new, safer battery technologies and the environment has been impacted through significant replacement of toxic cobalt by safer manganese.

Significance: **[text removed for publication]**.
St Andrews research on nanostructured **[text removed for publication]** electrodes has led to the development of a new generation of lithium batteries **[text removed for publication]**. These are particularly aimed at the vehicle market, **[text removed for publication]**.
Publication of a paper on the Lithium-air battery in 2006 resulted in an explosion of interest by companies worldwide (e.g. IBM, Toyota, Samsung) in this transformational energy storage technology.

Attribution and dates: The work was done in the laboratories of Professor Peter Bruce, and was completed between 1996 and the present day, and the impact is still ongoing.

Reach: The research has had global impact. The companies that have exploited the concepts **[text removed for publication]** are based in Asia (Japan, China), Europe and North America, and the impact on the consumer is also global in reach.

2. Underpinning research (indicative maximum 500 words)

The discovery of Lithium Manganese Oxide Electrode Materials First generation lithium-ion batteries used $LiCoO_2$ as the positive electrode material. Cost, safety and limitation of the quantity of Li that could be reversibly extracted from $LiCoO_2$ to 0.5 Li per formula unit, defined the need for new lithium intercalation hosts as cathodes. Prof. Bruce, a researcher at the University of St Andrews since 1991, was the first to synthesise layered $LiMnO_2$ (Nature, 1996 [1]) with the structure of $LiCoO_2$ but replacing Co by Mn, resulting in lower cost, improved safety and the ability to extract more Li than the $LiCoO_2$ material. $LiMnO_2$ had been targeted for several years by many groups but had not been prepared successfully. **[text removed for publication]**.

The key breakthrough in this research was the Bruce group's novel approach to the synthesis, which involved the formation of a different material, $NaMnO_2$, in the first instance, followed by an ion exchange step to replace the Na with Li [1] He further showed (in 2002) that partial replacement of Mn by other ions, including Ni and Al, improved stability. **[text removed for publication]**. The work on LMO electrode materials is protected in a series of patents (see for examples WO 97/26683 and WO 2003/009407).

Nanostructured Electrodes for Lithium Batteries Transforming the rate at which Li-ion batteries can be charged/discharged is essential for their use in electric vehicles (for so-called regenerative breaking). To attack this issue Bruce, in the early years of the 21st century, pioneered nanostructured intercalation electrodes, including TiO_2(B) nanowires/nanotubes and mesoporous

$LiMn_2O_4$ as anodes and cathodes respectively (2004/2008) [2,3]. He demonstrated that the combination of length scales in one material (micrometre, nanometre and atomic) endows materials with superior properties, and hence performance, compared with micron-sized particulate electrodes when used in lithium-ion batteries. **[text removed for publication]**. IPR is covered in US 12/857.431 and a Canadian patent application number CA 2.675.302.

The Lithium Air Battery Bruce is a pioneer of the rechargeable non-aqueous lithium-air battery (2006) [4], with a theoretical energy density 10 times greater than lithium-ion batteries of today and greater than lithium-ion batteries can ever achieve. He demonstrated that such a battery could be repeatedly recharged. By carrying out fundamental studies of the oxygen reduction mechanism at the positive electrode, he not only changed understanding of the science underpinning the non-aqueous lithium-air battery but also identified the crucial role of electrolyte stability. As a result of Bruce's work, many organisations are developing prototype lithium-air batteries. IPR in this area includes (PCT/JP2009/066856 and PCT/JP2010/059494).

The quality of Bruce's research in developing new concepts in solid state electrochemistry has been recognised by many international prizes, these include the Galileo Gallilei Award of the Electrochemical (Italy, 2012), the Arfvedson Schlenk Award of the German Chemical society (Germany 2011), the Carl Wagner Memorial Award of the US Electrochemical Society (2011), and the Akzo Nobel Science Award (UK, 2012) for '*outstanding contributions*' to electrochemistry and lithium battery technology. These awards recognised the impact Bruce's research has had on the technology as well as the quality of his underpinning research.

3. References to the research (indicative maximum of six references)

1. Synthesis of layered $LiMnO_2$ as an Electrode for Rechargeable Lithium Batteries, A. R. Armstrong and P. G. Bruce, *Nature*, **381**, 499-500 (1996). DOI: 10.1038/381499a0 (cited 863 times)
2. TiO_2-B Nanowires, A. R Armstrong, G. Armstrong, J. Canales and P. G. Bruce, *Angew. Chem. Int. Ed.*, **43**, 2286-2288 (2004). DOI: 10.1002/anie.200353571 (cited 418 times)
3. Synthesis of Ordered Mesoporous Li-Mn-O Spinel as a Positive Electrode for Rechargeable Lithium Batteries, F. Jiao, J. Bao, A. H. Hill, P. G. Bruce, *Angew. Chem. Int. Ed.,* **47**, 9711-9716 (2008). DOI: 10.1002/anie.200803431 (cited 94 times)
4. The Rechargeable Li_2O_2 Electrode for Lithium Batteries, T. Ogasawara, A. Debart, M. Holzapfel and P. G. Bruce, *J Am Chem. Soc.*, **128**, 1390-1393(2006). DOI: 10.1021/ja056811q (cited 334 times)

4. Details of the impact (indicative maximum 750 words)

The work at St Andrews has impacted on the materials, battery, electronics and automotive industries here in the UK and worldwide, bringing economic, consumer and environmental benefits globally. The beneficiaries are wide-ranging: **[text removed for publication]**. In addition, the **[text removed for publication]** nanostructured electrodes have had particularly strong impact on companies (**[text removed for publication]**) that are targeting the automotive industry and there are vehicles that now contain this technology (**[text removed for publication]**). Finally, the development of the lithium-air battery has had significant impact on several companies, who are looking to develop very high power 3rd generation lithium battery materials [S2, S5].

A. Economic Impact. The concepts described in the research above have had significant impact on a number of different areas of lithium battery technology but in particular it has impacted on the development of 2nd generation rechargeable Li-ion batteries produced by all the major battery manufacturers globally, **[text removed for publication]**.

The discovery and synthesis of layered $LiMnO_2$ (LMO) as a positive electrode for lithium batteries **[text removed for publication]** to reduce cost and improve safety. These materials are manufactured worldwide, as are the batteries that use them as positive electrodes. The value of the lithium battery market is estimated at $12 billion per annum (approx. 4 billion cells) and the Mn based share at ~40% [S6]. **[text removed for publication]**

The University of St Andrews patented the original work and the IPR was licensed to Nissan Chemicals for a significant period. However, it is the general concept that has had the most impact. The wealth of possible combinations of elements in mixed metal $Li(Mn_{1-x}M_x)O_2$ materials means that each company has developed their own particular electrode. **[text removed for publication]**.

The director of LIB Battery Consultants LTD, writes that Peter Bruce's work on "…*manganese-based lithium oxides has made a major impact in the field. His work on the spinel materials laid the foundations for their later use as cathodes in lithium ion batteries for automotive applications, for example in the Nissan leaf and Vauxhall Ampera."* [Reference S1]

II. The hierarchical approach to lithium-ion battery electrode design, combining, nano and micron scales, demonstrated by Bruce, is being exploited in the fabrication of titanate anodes for lithium-ion batteries **[text removed for publication]**. The advantage is that the batteries can be safely charged and discharged at higher rates than traditional lithium-ion batteries, because the nanostructure enhances the charge/discharge rates, while the hierarchical structure ensures that the electrode is more dense than a simple powder of nanoparticles, thus delivering high volumetric capacity. Nanostructured lithium titanate batteries account for only a small percentage of the total lithium battery market as yet, but their market share is predicted to increase over the next ten years substantially.

III. The theoretical energy density (storage) of the lithium-air battery is 10 times greater than lithium-ion batteries of today and greater than Li-ion batteries can ever achieve. As such, lithium-air could deliver the Holy Grail in the automotive industry of an electric vehicle with a 500km driving range. Bruce's pioneering studies in 2006 led directly to an explosion of interest in the Li-air battery, not only in academic research but also within industry. The major current impact (2009 onwards) of this relatively recent research advance is on companies, who are actively developing the concepts behind the lithium-air battery. The Economist [See reference S2] reported that the advances "..*that Dr Bruce's team has designed can be a mere one-eighth to one-tenth the size and weight of modern batteries, while still carrying the same charge. Making such a battery is also expected to be cheaper. Lithium cobalt oxide accounts for 30% of the cost of a lithium-ion battery. Air, however, is free."* Since then major automotive companies around the world are pursuing the technology. Examples of companies developing the Li-air battery are, IBM, Toyota/BMW, CEA (France), BASF/Bosch Germany, Volkswagen, Samsung. IBM has announced they will demonstrate a prototype in 2014, [See corroborative references S5, S9].

B. Policy Impact

A significant role as advocate and advisor to industry and Government has arisen from the research on lithium batteries at St Andrews. Bruce has appeared before a Parliamentary Select Committee. Importantly, Bruce Chaired a Royal Society of Chemistry committee that produced a report on Energy Storage, **[text removed for publication]**.

C. Societal Impact

Lithium batteries have become firmly entrenched in consumer goods over the last decade. As such the impact of the fundamental research described above and its subsequent exploitation has played an important part in the impact of 2nd generation lithium batteries on society across the world. For the LMO battery technology the impact has allowed safer power tools and medical device batteries, and nanostructured electrode batteries are breaking into the electric vehicle market. **[text removed for publication]**.

5. Sources to corroborate the impact (indicative maximum of 10 references)

F1 Corroborative Letter from director of LIB Battery Consultants LTD, **[text removed for publication]**

S2 The Economist: Air Power http://www.economist.com/node/14299690 which corroborates the Bruce contribution to the lithium air battery.

[text removed for publication]

S4 Toshiba Lithium titanate SCIB technology http://www.toshiba.com/ind/product_display.jsp?id1=821

S5 Announcement of Toyota/BMW lithium air battery: http://paultan.org/2013/01/25/toyota-bmw-jointly-research-lithium-air-batteries-fuel-cell-system-and-sports-car-also-on-the-cards/

S6 Lithium Battery market http://www.frost.com/prod/servlet/press-release.pag?docid=274194514

S7 Explanation of lithium manganese oxide battery and major uses http://batteryuniversity.com/learn/article/types_of_lithium_ion

S8 Report that Toshiba SCIB lithium titanate battery will be used in the Mitsubshi electric vehcle http://www.engadget.com/2011/06/16/toshiba-scib-to-be-used-in-mitsubishi-i-miev-recharge-to-80-per/

S9 Announcement of IBM lithium-air battery protoytype http://www.bloomberg.com/news/2013-02-21/lithium-air-battery-gives-ibm-hope-of-power-without-fires.html

S10. Royal Society of Chemistry: Electrochemical Energy Storage: a vision for the future, 2010. Corroborating the new policy initiative from BIS.

http://news.bis.gov.uk/Press-Releases/Multi-million-boost-for-UK-electric-vehicle-battery-technology-67f95.aspx