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ABSTRACT

This paper is a personal reflection of 20 years of sodium- and lithium-based battery R&D in South Africa between 1974 and 1994. The impact of the innovative materials science and engineering research conducted during this period is highlighted by the later successful implementation of batteries in powering practical systems, as well as in technology licensing.

KEYWORDS

CSIR, battery, Zebra, sodium-metal chloride, sodium-sulphur, LiAl/FeS_x, lithium-ion, spinel.

Table of Contents

1. Introduction	61
2. Sodium Batteries – the Zebra Battery	61
3. Lithium Batteries – Materials Innovation and the Exploitation of Intellectual Property	63
4. Conclusion · · · · · · · · · · · · · · · · · · ·	65
Acknowledgements	66
References ·····	66

1. Introduction

In 1974, at the time of the first 'oil crisis' when the price of oil jumped from \$3 to \$12 a barrel, Johan Coetzer, a structural chemist, returned from a year's farming in Pongola, Natal, to resume his scientific career at the Crystallography Division of the National Physical Research Laboratory, Council for Scientific and Industrial Research (CSIR), in Pretoria, South Africa (Fig. 1). The effect of the oil embargo by Arab countries against the United States, Western countries and Japan for their support of Israel triggered a worldwide awareness of the need for alternative energy sources and improved batteries for energy storage.

The oil crisis prompted Coetzer to initiate structural studies of battery materials. New to the field of solid state electrochemistry, Coetzer embarked on an investigation of the structure-electrochemical properties of silver iodide-amine iodide solid electrolytes that showed anomalously high Ag⁺-ion conductivity at room temperature.¹ This project heralded the start of a 20-year period when CSIR and South Africa would make major contributions to advancing international battery science and technology.

When Michael Thackeray joined Coetzer in 1975, he used the silver iodide project for his PhD thesis,² while Coetzer turned his attention to more practical technologies. The discovery of the Na⁺-ion conducting solid electrolyte, ' β -Al₂O₃', by Weber and Kummer at Ford Motor Company in 1967 had opened the door to the possibility of developing a non-aqueous, high-energy, and high-temperature (350 °C) sodium-sulphur (Na/S) battery to replace lead-acid and nickel-cadmium batteries, particularly for electric vehicles and stationary energy storage.³ In the Na/S system, the molten sodium and sulphur electrodes are separated by a thin ' β -Al₂O₃' solid electrolyte membrane. By 1975, development of this system was well under way in the United States and Europe. At the same time, another high-temperature battery,

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based on a lithium aluminum-iron sulphide (LiAl/FeS₂) electrochemical couple and a molten salt (LiCl,KCl) electrolyte, was under development at Argonne National Laboratory in the USA.^{3,4} In this system, two solid electrodes, LiAl and FeS₂, are separated by a liquid electrolyte. Questions at that time were: 1) would the ultimate answer to energy storage lie in high temperature sodium- or lithium-based batteries and, 2) if so, would the liquid-solid-liquid configuration of the Na/S battery be preferable to the solid-liquid-solid configuration of the LiAl/FeS₂ system?

Because molten sodium and sulphur are highly reactive and combine violently if the ceramic ' β -Al₂O₃' solid electrolyte in Na/S cells ruptures, and because molten sulphur is highly corrosive, Coetzer proposed the idea of using the pores within zeolitic structures to immobilize and contain the sulphur in a solid electrode matrix, thereby enhancing safety and minimizing corrosion. This concept was first evaluated in high-temperature LiAl/LiCl,KCl/zeolite-sulphur cells using Argonne's cell configuration. This study prompted Coetzer to consider alternative electrodes for Argonne's technology and his thinking moved away from FeS₂ and zeolite-sulphur to iron chloride electrodes, the initial studies being conducted on chlorinated iron carbides, 'Fe_xCCl_y', and, subsequently, simply iron dichloride, FeCl₂^{5,6} Meanwhile, Thackeray broadened the scope of the research by initiating an exploration of less corrosive metal oxides as alternatives to iron sulphide and iron chloride electrodes in hightemperature lithium cells, notably those from the family of stable iron oxides such as Fe₂O₃ and Fe₃O₄.^{7,8}

2. Sodium Batteries - the Zebra Battery

The early battery work and the ideas being generated at CSIR did not go unnoticed. In 1976, Coetzer elicited the interest of industry and, in particular, Roger Wedlake of De Beers who, recognizing the future potential of electric vehicles, persuaded senior management at De Beers and Anglo American Corporation

M. Thackeray, S. Afr. J. Chem., 2011, **64**, 61–66, <http://journals.sabinet.co.za/sajchem/>.

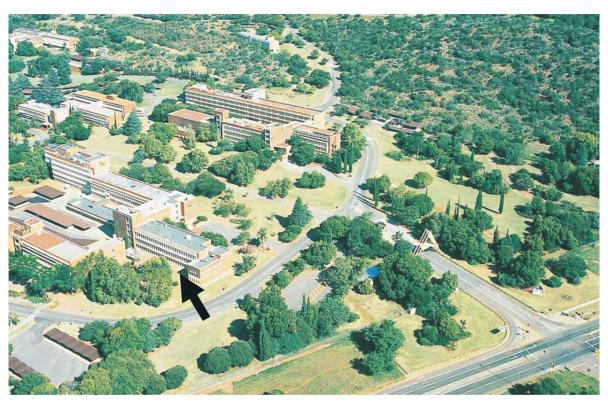


Figure 1 An aerial view of CSIR, Pretoria, South Africa, showing the National Physical Research Laboratory (arrowed), where the initial sodium and lithium battery research was conducted (courtesy of CSIR).

to invest in CSIR's battery initiatives along with the South African Inventions Development Corporation (SAIDCOR) that was affiliated with CSIR. In 1977, a formal agreement between CSIR, SAIDCOR, De Beers and Anglo American to undertake high-temperature battery research and development (R&D) was signed. Significant progress was made, and within two years, several key patents had been filed internationally; potential partners abroad were identified to help drive CSIR's battery technologies forward. In 1979, visits were made to Argonne National Laboratory, USA, and to the Atomic Energy Research Establishment (AERE) at Harwell, UK, where the Li/FeS, and Na/S technologies, respectively, were in advanced stages of development. Argonne declined the offer to collaborate, ostensibly because of the political sensitivities in South Africa at the time. On the other hand, Ron Dell and Roger Bones at Harwell, who had participated with British Rail in the development of Na/S batteries, sensing the technological and safety limitations of the Na/S system, welcomed the South African delegation in anticipation of developing an alternative system, despite the political embargoes against the country at the time. A huge advantage of the early collaboration with AERE, Harwell, was that it gave CSIR scientists immediate access to sodium-sulphur technology that enabled the evaluation of CSIR's zeolitesulphur and iron-chloride electrodes in the sophisticated sodium-sulphur battery configuration.

The political isolation of South Africa and international scientific and trade boycotts against the country made it difficult for De Beers/Anglo American and particularly CSIR, a government-owned research institution, to operate openly with Harwell and Beta R&D. For this reason, the scientific collaboration was undertaken without public exposure. The project was code-named 'Zebra' for 'Zeolite Battery Research in Africa'.⁹ Because the zeolite-sulphur electrode was solid, a molten salt NaAlCl₄ electrolyte (m.p. = 155 °C) was added to the electrode compartment to enable rapid Na⁺-ion diffusion between the zeolite-sulphur and sodium electrodes via the solid ' β -Al₂O₃' electrolyte. The early results on Na/zeolite-sulphur cells were not promising, largely because the zeolite component added considerable extra weight to the system, thereby yielding lower energy per unit mass compared to the pure Na/S battery.

Fortunately, the sodium-sulphur battery configuration was also suitable for evaluating the iron chloride electrodes being developed by Coetzer and his team for the Argonne-type high-temperature lithium battery.^{5,6} In the sodium cell configuration, the reaction is simply:

$$2 \operatorname{Na} + \operatorname{FeCl}_2 \rightarrow 2 \operatorname{NaCl} + \operatorname{Fe} \tag{1}$$

It was Roy Galloway at CSIR who first realized and demonstrated that, unlike LiAl/FeS_x, LiAl/FeCl₂ and Na/S cells that are assembled in the charged state with highly reactive LiAl and Na negative electrodes (anodes), CSIR's sodium-iron chloride cells could be assembled in the discharged state using a simple mixture of table salt (NaCl) and iron metal powders in the positive electrode (cathode), thereby circumventing the difficulty and hazards of handling LiAl alloy or metallic sodium.^{10,11} Galloway also showed that the Na/NiCl₂ electrochemical couple offered a slightly higher cell voltage (2.58 V) and was more stable than the Na/FeCl₂ couple (2.35 V) to electrochemical cycling, making it the preferred system. Despite the demise of CSIR's Na/zeolite-sulphur technology, the name 'Zebra' persisted and is still in use today to describe sodium-metal chloride batteries, although the acronym was temporarily changed to represent 'Zero Emission Battery Research Activity'.

Significant progress was made by CSIR and Harwell in the early 1980s in demonstrating the feasibility of sodium/metal chloride battery technology. In 1982, recognizing the need to scale up the production and expedite the evaluation of Zebra batteries in electric test vehicles, Anglo American acquired facilities in Derby, UK, and established the company Beta R&D to manufacture ' β -Al₂O₃' tubes, cells, and batteries under the





Figure 2 Mercedes 'A'-class electric vehicle in California (left) and in the Arctic (right) (reproduced with permission from Ref. 1).

management of Jim Sudworth, a pioneer of Na/S technology from British Rail.¹² By 1984, a multi-kWh Zebra battery had been built and demonstrated in an electric vehicle.

By 1984, therefore, the Zebra project had made excellent technological progress. Anglo American's growing confidence and investment in a project with huge industrial potential and significance led to their establishment of a new facility, Zebra Power Systems, outside Pretoria with Johan Coetzer as managing director. The transfer of the project to industry with most of the CSIR team joining the Anglo American operation gave CSIR the opportunity in 1986 to divest from the Zebra battery initiative and sell its share of investments, while maintaining its links with the project through contract research. Thackeray decided to remain at the CSIR where he and Keith Adendorff continued to provide R&D support to Anglo American/Zebra Power Systems. Over the next 15 years in a joint effort between Zebra Power Systems, Harwell, Beta R&D, and Daimler Benz, Germany, outstanding progress was made in optimizing Zebra battery technology and demonstrating it in electric vehicles in all weather climates (Fig. 2). Of particular note was that the technology was successfully used in Mercedes buses to transport athletes within the Olympic Village at the 1992 Games in Barcelona.

Sadly, after 20 years of technological innovation and success, both Anglo American and Daimler Benz decided to withdraw from further development of the Zebra battery, evidently because of the lack of a worldwide electric vehicle infrastructure that would sustain the technology. This divestment came a few years after the United States Department of Energy had also decided to terminate its high-temperature battery R&D initiatives for transportation, notably Argonne's LiAl/FeS_x system that had been under development in a joint programme with SAFT America for several years⁴. The decision by Anglo American and Daimler Benz to terminate their development of the Zebra battery also coincided with the demise of GM's all-electric vehicle, EV1, which occupied an unprofitable niche of the car market; by 1999, only 800 EV1 units had been leased over four years with production costs of \$1 billion.¹³ In 1999, the entire Zebra operation was sold to MES-DEA, Switzerland,12 where a limited number of batteries for electric vehicles and stationary applications are currently being manufactured by a newly constituted company, FZ Sonick SA, formed between FIAMM and MES-DEA.^{12,14} In 2007, Rolls-Royce Marine chose the Zebra battery as the propulsion source for the NATO rescue submarine.¹⁵ In the same year, General Electric acquired Beta R&D, which enabled rapid advancement and the early production of Zebra-based 'Durathon' battery products.¹⁶ GE's targeted applications include 1) an uninterruptible power supply for systems that require continuous supply of power, 2) energy storage for telecom and utility industries, and 3) advanced transportation systems such as heavy-duty hybrid-diesel locomotives.

3. Lithium Batteries – Materials Innovation and the Exploitation of Intellectual Property

During the early years of the Zebra project at CSIR in the late 1970s, Thackeray initiated studies of high-temperature LiAl/ LiCl,KCl/iron oxide cells to evaluate their performance against Argonne's more corrosive LiAl/LiCl,KCl/iron sulphide system. In these studies, which included the screening of a wide number of other metal oxides, it was observed that the family of iron oxides, notably Fe2O3 with a corundum-type structure and Fe₃O₄ with a spinel-type structure, provided far superior electrochemical performance than other metal oxide electrodes.^{8,17} Another observation was that when the lithium cells were continuously discharged and charged, an iron oxide structure with spinel-type features was obtained in fully-charged cells, irrespective of the structure-type of the parent electrode material. The voltage of these high-temperature LiAl/iron oxide cells was too low, with most of the discharge occurring at about 0.9 V, to be competitive with the Na/S (2.1 V) and LiAl/FeS_x (1.7 V) systems and, therefore, received relatively low priority in CSIR's battery research programmes.

By 1980, primary (i.e. non-rechargeable) lithium batteries that operated at room temperature were beginning to enter the market in consumer products, such as calculators, watches and cameras; primary lithium batteries were also under development for military applications. Thackeray took the opportunity, with financial support from CSIR, SAIDCOR and Anglo American, to travel to the Inorganic Chemistry Laboratory at Oxford University, UK, where high-level lithium battery research was being undertaken by Professor John Goodenough, a world-renowned authority in the field, to learn the trade and to evaluate the room-temperature electrochemical behaviour of the most promising metal oxide electrode materials that had been identified at CSIR in high-temperature cells. One year before Thackeray's visit, Goodenough had published (and patented) the concept of using a layered LiCoO₂ electrode structure for lithium cells; this material was later to become the cathode of choice for the first generation of rechargeable lithium-ion battery products.18,19

In the autumn of 1981, Thackeray arrived at Oxford with several spinel samples in his possession, including magnetite (Fe_3O_4) and hausmannite (Mn_3O_4) , where he immediately launched an investigation of their chemical and electrochemical reactions with lithium at room temperature. Despite the robust, gem-like properties of the spinel structure (that takes its name from the semi-precious mineral *'spinel'*, MgAl₂O₄), and to Goodenough's surprise, Thackeray demonstrated that it was

M. Thackeray, *S. Afr. J. Chem.*, 2011, **64**, 61–66, <http://journals.sabinet.co.za/sajchem/>.

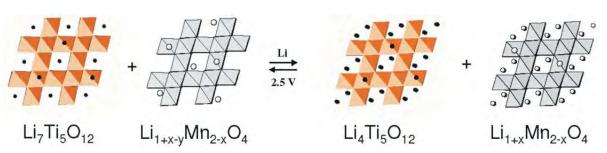


Figure 3 Schematic illustration of a Li₄Ti₅O₁₂/Li_{1+x}Mn₂-_xO₄ 'spinel-spinel' lithium-ion cell

possible to insert lithium into both Fe_3O_4 and Mn_3O_4 . Subsequent structural refinements undertaken together with Bill David, a post-doctoral student in Goodenough's group at the time, showed that the $[Fe_2]O_4^-$ and $[Mn_2]O_4$ framework of the Fe[Fe2]O4 and Mn[Mn2]O4 spinel structures remained intact during lithium insertion, resulting in the rocksalt products LiFe[Fe₂]O₄ and LiMn[Mn₂]O₄, respectively.^{20,21} During the electrochemical reactions, the Fe and Mn ions within the interstitial space of the spinel framework were displaced into neighboring crystallographic sites to make room for the incoming lithium ions. These findings and the recognition by Goodenough (who was well acquainted with spinel structures from his pioneering work in the 1950s on their magnetic properties) that the $[Fe_2]O_4$ and [Mn₂]O₄ spinel framework provided a three-dimensional interstitial space for Li⁺-ion diffusion had immediate implications - it led rapidly to the investigation of the lithium spinel Li[Mn₂]O₄ system,²¹ in which lithium could diffuse more rapidly within the structure than in Fe₃O₄ and Mn₃O₄. Because the discoveries at Oxford University had originated from CSIR's ideas and spinel battery projects, Goodenough graciously agreed to give SAIDCOR title to the international patent that was filed on the use of the $[M_2]O_4$ spinel framework (M=metal ions) as an insertion electrode for lithium cells and batteries.²²

Thackeray returned to CSIR at the end of 1982 and established a team to expand CSIR's research activities on the electrochemical properties of transition metal oxide electrodes in room-temperature lithium cells. With 1) the departure of the Zebra project from CSIR in 1986, 2) Anglo American's focus and commitment to the industrial development and commercialization of hightemperature sodium/metal chloride batteries, and 3) CSIR's decision to withdraw from the industrialization process, control of the lithium battery patent portfolio that had been initiated at CSIR was released by Anglo American and fully vested in Technifin, a company established by CSIR to replace SAIDCOR, 50% of which was owned by CSIR and 50% by the Industrial Development Corporation (IDC) of South Africa.

By the late 1980s, despite the unsuccessful attempt by Moli Energy, Canada, to commercialize a rechargeable lithium battery with a metallic lithium anode that resulted in fire-related incidents, there were strong signals from the lithium battery industry in Japan that significant progress was being made to overcome the safety limitations of the Moli Energy cells. Moreover, it became apparent that LiMn₂O₄ spinel electrodes were receiving considerable attention by Sony Corporation and Sanyo Electric Company. Thackeray and his team, therefore, intensified their research to design and patent novel manganese oxide electrode structures,23 which offered greater long-term prospects than the relatively unstable and higher cost LiCoO₂based (and LiNiO₂-based) electrode systems pioneered by Goodenough^{18,19}; the strategy, which ultimately proved successful, was to target stabilized manganese oxides with one-dimensional tunnels for lithium-ion transport,24,25 layered manganese oxide structures that offered two-dimensional lithium diffusion,26-28

and spinel-related manganese-oxide structures with a three-dimensional interstitial space for lithium. $^{\rm 29,30}$

In 1991, Sony Corporation introduced the first commercial, rechargeable lithium-ion cells into the market. In order to reduce the safety hazards of the lithium metal anode, Sony applied the same principle that had been used in the sodium/metal chloride Zebra cells, i.e. assemble the lithium-ion cells in the discharged state. In this case, the lithium was initially contained within a LiCoO_2 cathode structure in the same manner as sodium is contained in the NaCl structure of a discharged Zebra cathode.

Instead of plating metallic lithium at the anode during charge, Sony used carbon (typically graphite, C_6) as a host structure to accommodate the lithium, thereby significantly enhancing the safety of the cell. The reversible lithium insertion/extraction reaction that takes place during operation of the Sony lithiumion cell is represented as:

$$Li_{x}C_{6} + Li_{1-x}CoO_{2} \Leftrightarrow C_{6} + LiCoO_{2}$$

$$(2)$$

in which x_{max} is approximately 0.5. During charge and discharge of the cell, which occurs at approximately 4 V, the lithium ions shuttle between the anode and cathode host structures, hence the name '*lithium-ion*' cell. A similar reaction occurs in cells with a LiMn₂O₄ spinel cathode:

$$Li_{x}C_{6} + Li_{1-x}Mn_{2}O_{4} \Leftrightarrow C_{6} + LiMn_{2}O_{4}$$
(3)

Reaction (3) also occurs at 4 V, making $LiMn_2O_4$ a particularly attractive alternative to the more expensive LiCoO2. However, LiMn₂O₄ electrodes were observed to dissolve and lose electrochemical capacity (energy) during electrochemical cycling, which precluded their widespread use in lithium-ion cells. By slightly modifying the composition of the spinel electrode to increase the Mn⁴⁺ content in the structure, for example, as in the lithium-rich spinels $\text{Li}_{1+x}\text{Mn}_{2-x}O_4$ (0 < x \leq 0.33), Gummow, de Kock and Thackeray showed that it was possible to suppress solubility as well as severe structural distortions in the spinel electrode, leading to significantly improved electrochemical performance.^{29,30} At about the same time, Ferg, Gummow, de Kock and Thackeray³¹⁻³³ demonstrated that safe lithium-ion cells could be constructed by coupling a Li₄Ti₅O₁₂ spinel anode with a stabilized Li_{1+x}Mn_{2-x}O₄ spinel cathode; in this case, the lithium ions shuttle between two metal oxide structures at 2.5 V (Fig. 3). These inventions complemented the original Thackeray and Goodenough spinel patent, and they significantly strengthened CSIR's growing internationally-lodged patent portfolio on lithium battery electrode materials.

The introduction of the first commercial lithium-ion batteries by Sony Corporation triggered a series of visits in 1992 and 1993 by Ora Safriel of Technifin and Thackeray to various battery companies in Japan, Europe and the United States in an attempt to gauge interest in, and exploit, CSIR's lithium battery patent portfolio. These visits heralded the start of a successful licensing campaign, particularly with the major Japanese lithium battery manufacturers. The first license was executed in 1995 and others

M. Thackeray, S. Afr. J. Chem., 2011, 64, 61-66, <http://journals.sabinet.co.za/sajchem/>.

(a)



Figure 4 (a) Nissan's all-electric car, the Leaf, and (b) GM's range-extended electric car, the Chevy Volt, powered by lithium-ion batteries and commercialized in 2010. Source: Wikimedia - Permission for reuse released by Tennen-Gas and IFCAR, respectively.

followed, generating significant royalty income for CSIR/Technifin over the next several years.

In 1992, after supporting lithium battery research for approximately 10 years, CSIR management decided to terminate its investment in this field, supposedly because of the lack of a lithium battery industry in South Africa. They were unaware of the full significance of the research being undertaken on the CSIR campus and did not foresee the impending impact of lithium battery technology that was to follow during the consumer electronics boom in the 1990s. Thackeray, sensing a bright future for lithium battery technology and receiving an offer to continue his materials-related lithium battery research at Argonne National Laboratory, left CSIR for the United States in January 1994. The battery group that remained at CSIR continued to operate for another year before closing down its operations.

Besides its cornerstone spinel patents, CSIR's patent portfolio covered layered MnO₂ electrodes derived by partially removing Li₂O from a layered Li₂MnO₃ (Li₂O•MnO₂) precursor by acid treatment.²⁷ Although this reaction was accompanied by some H⁺-ion exchange for Li⁺ ions, relithiation of the chemically delithiated product reversed the ion-exchange process irreversibly in a non-aqueous lithium electrochemical cell. The electrochemical properties and composition of a typical discharged electrode produced by this method, Li_{1.09}Mn_{0.91}O₂ (or, in alternative notation, 0.2Li₂MnO₃•0.8LiMnO₂), were reported by Rossouw, Liles and Thackeray between 1991 and 1993;²⁸ the results highlighted the important role that the unreacted layered Li₂MnO₃ component played in stabilizing the layered MnO₂ component in the overall electrode structure. This foundational research at CSIR subsequently paved the way for the later design by Thackeray's team at Argonne National Laboratory of highcapacity composite electrode structures, xLi₂MnO₃•(1-x)LiMO₂, in which M is predominantly Mn and Ni.^{34,35} Lithium batteries containing Argonne's patented materials are currently being licensed and commercialized worldwide, not only for portable electronic devices but also for larger scale transportation applications.

After leaving CSIR, Thackeray continued to provide technical support as a consultant to CSIR/Technifin to secure and defend important patents within the portfolio. Over recent years, Johan Hattingh, who replaced Ora Safriel on her retirement as Managing Director of Technifin in 2005, has proactively ensured the defense and successful grant of the remaining cornerstone patent applications on lithium manganese oxide spinel cathodes and lithium titanium oxide spinel anodes, particularly in Japan³² and the United States.³³ The grant of these key patents has led to further successful licensing of CSIR's spinel technology. Negotiations between CSIR/Technifin and lithium battery companies worldwide are still ongoing, which augers well for future licenses until the patents expire in the 2013–2017 timeframe.

Since their introduction into the world market in 1991 to power consumer electronics, lithium-ion batteries have become a strategic resource. They are now found in a myriad of applications from portable telecommunications, laptop computers, and power tools to medical, defence, and aerospace devices.³⁶ During the past decade, lithium-ion battery technology has made inroads into the transportation sector; it is used to power electric bikes and is being targeted for the mass-market production of hybrid, plug-in hybrid, and all-electric vehicles in the near to longer term;³⁷ lithium-ion batteries are also being developed for energy storage in large stationary systems, such as uninterrupted power supply units. With the anticipated growth in these market sectors, rechargeable lithium-ion batteries are likely to constitute a significant 'lithium economy'. CSIR's spinel technology is particularly attractive for high-power applications, such as hybrid-electric vehicles, because the [M₂]O₄ spinel framework with its three-dimensional interstitial space for lithium-ion transport can withstand exceptionally high currents compared to other metal oxide electrodes used in commercial lithium-ion cells, such as LiCoO₂ (layered structure). It must be particularly rewarding to CSIR that the first commerciallyavailable lithium-battery powered electric cars, the Nissan Leaf (Fig. 4a) and General Motor's Chevy Volt (Fig. 4b), released to the general public in 2010, both operate with lithium-manganeseoxide spinel as a major cathode component in the batteries.

4. Conclusion

The contributions made by Coetzer and Thackeray to advancing battery science and technology were recognized at the opening ceremony of South Africa's Science Park, The Innovation Hub, in Pretoria in 2005. In retrospect, one cannot help but wonder: What would have happened if Anglo American and CSIR had decided to invest in both sodium and lithium battery technologies over the longer term? The extraordinary advances in lithium battery technology over the past 20 years have opened up vast opportunities for market growth. With 1) current oil prices at approximately \$100 per barrel, and 2) the need to reduce CO₂ emissions and other greenhouse gases, the requirement for increased energy efficiency afforded by lithium batteries and by Zebra batteries in more selected applications, particularly in the transportation and stationary energy storage sectors, is expanding. The necessity for improved electrochemical energy storage is now clearly receiving the urgent attention it failed to get during the 1990s, particularly in the western hemisphere. The foundational research conducted at CSIR in the 1980s, on both sodium and lithium battery technologies, was clearly ahead of its time.

Acknowledgements

Several colleagues and acquaintances have expressed interest in learning about the history of South African battery research that was initiated at CSIR approximately 35 years ago – this paper is the result. Roy Galloway (formerly at CSIR, South Africa and Beta R&D, UK) and Jim Sudworth (formerly at Beta R&D, UK) of General Electric are thanked for proof-reading the manuscript and providing input to the Zebra battery narrative. Professor Alan Morris of the University of Cape Town is thanked for valuable discussions. Support to write this article from the Office of Vehicle Technologies, U.S. Department of Energy, is gratefully acknowledged.

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