



University of Jaffna

Professor Sivapathasuntharam Mageswaran
Memorial Lecture - 2024



**“Energy Storage Devices and
the Challenging Role of the Chemist”**

by

Prof. H.M.N. Bandara,
Retired Senior Professor in Chemistry,
Department of Chemistry,
University of Peradeniya,
Sri Lanka.

on

Tuesday 15th October 2024
at 03.30 p.m

at

Kailasapathy Auditorium,
University of Jaffna.



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Professor Sivapathasuntharam Mageswaran
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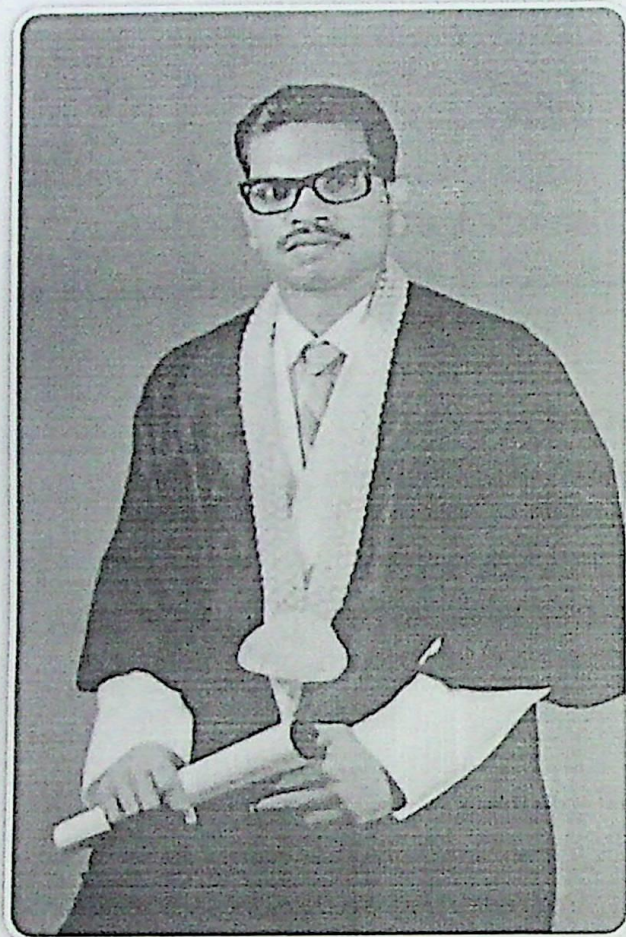
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Prof. Sivapathasuntharam Mageswaran

பேராசிரியர். சிவபாதசுந்தரம் மகேஸ்வரன்

Messages from the Vice Chancellor



It is my great pleasure and honor to welcome all the participants to this 26th year commemoration of Late Professor Sivapathasuntharam Mageswaran, who was the Dean of the Faculty of Science for two consecutive terms.

Our University of Jaffna was inaugurated in 1974 and the Golden Jubilee Celebrations are celebrated throughout the 2024 year with all sphere of events. In this respect, Professor Sivapathasuntharam Mageswaran Memorial Lecture -2024 becomes highly significant.

Professor S. Mageswaran, was born in Kokuvil on the 28th of March 1942 and had his school education at the J/Kokuvil Hindu Collage. He entered the University of Ceylon in 1962 and awarded a Bachelor of Science Honors degree in Chemistry in 1966. He joined the University of Peradeniya as an Assistant Lecturer in 1966 and served there upto 1975. During this period, he completed his MSc and PhD degrees at the University of Sheffield, United Kingdom in 1969 and 1972 respectively.

Professor Mageswaran joined the Faculty of Science of the newly established University of Jaffna as one of its pioneers on 19th May 1975 and served there until his untimely demise on 2nd February 1998. He was the founding Head of Department of Chemistry and was promoted to Professor of Chemistry in 1979 and Senior Professor of Chemistry subsequently in recognition of his contribution to the academic, administrative and research activities at this University. Further, he served as the Dean of the Faculty of Science for two consecutive terms and guided the Faculty during the period 1991-1996. He also functioned as an elected member to the Governing Council of the University and the Management Committee of the Vavuniya Campus of the University of Jaffna.

Prof. Mageswaran played a pivotal role in shaping this institution into a strong academic entity. As the founding Head of the Department of Chemistry, he worked tirelessly to produce graduates of outstanding quality. He faced a lot of constraints during the most difficult periods in the region as well as in the University and overcame the all challenges through his diligent effort and dedication. He has devoted his life for the development of the Faculty and the University of Jaffna and served as a Chairperson/Active Member of several selections boards, standing Committee ad hoc Committees and authorities of the University of Jaffna. Following his untimely demise on 2nd February 1998, The University of Jaffna honored him with an honorary degree of Doctor of Science. Posthumously at the 16th Convocation held on 4th October

1998. Further, to honor his valuable contributions the University of Jaffna named the chemistry building as the Mageswaran chemistry building as the "**Mageswaran block**" following his demise in 1998.

The Professor Mageswaran commemorative committee of the Faculty of Science instituted the above Memorial Lecture from 30th of March 1999 and consecutively conducted every year by the University of Jaffna to commemorate the services of late. Prof.Mageswaran. This year we are delighted to have Prof.H.M.N.Bandara, Retired Senior Professor in Chemistry Department of Chemistry, University of Peradeniya to deliver this memorial oration of late Prof.S.Maheswaran under the title of "Energy Storage devices and the challenging role of the chemist " Prof H.M.N Bandara served as a Senior Professor in Chemistry at the Department Chemistry ,University of Peradeniya. He earned his Bachelor of Science honours in Chemistry degree in 1971 from the University of Ceylon and also awarded the B.Z.F.Khan gold medal for best performance in the final examination. He commenced his professional career as an Assistant Lecturer in Chemistry in the Peradeniya Campus of the then University of Ceylon. During this period, he obtained his PhD degree in Inorganic Chemistry (1977) from the University of Aston, Birmingham, United Kingdom. On successfully completion of his Doctoral Degree, he continued to serve at the Department of Chemistry, University of Peradeniya and later promoted as senior lecturer in 1982, Professor in Inorganic Chemistry in 1990 and Senior Professor in Inorganic Chemistry in 1998.

He is a research focused person and authored more than 100 scholarly publications and research articles in international refereed Journals. He has retired from the University service in 2013 and continuing research activities in the area of energy storage devices.

On behalf of the University of Jaffna, I would like to extend our appreciation, to Prof.H.M.N.Bandara for accepting our kind invitation and delivering the late Prof.S.Mageswaran Memorial Lecture for the year 2024, from his expertise area of research. I hope his talk on "Energy Storage devices and the challenging role of the chemist" will create new thoughts and ideas in the relevant field. Once again I thank Prof.Bandara for accepting our invitation and delivering this memorial oration-2024.

All glories to almighty God.

Prof.S.Srisatkunarajah,
Professor in Mathematics,
Vice Chancellor,
University of Jaffna.

Ladies and Gentlemen,

First of all, I am honoured to be invited to deliver this Professor S. Mageswaran Memorial Lecture today. I can recollect that Professor Mageswaran was on the staff of the Department of Chemistry, University of Peradeniya during early 1970's. However, his stay at Peradeniya was quite short. In the year 1970, I was in the third year of the Chemistry Special degree course. I remember that he was the supervisor for my Seminar Presentation on "Perfluoro Ligands in Coordination Chemistry".

I take this opportunity also to remember Professor Mrs. Mageswaran, with whom I had a longer association, as we were serving together on the setting panel in Chemistry for the G.C.E. (Advanced Level) examination during the period 2000-2010.

Prof. H. M. N. Bandara
Department of Chemistry
University of Peradeniya,

Energy Storage Devices and the Challenging Role of the Chemist

Energy, in many of its forms has become an essential utility for human existence. The enormity of this energy requirement is amply evident from the following data.

Global energy production / year = 170,000 TWh

Number of petroleum oil barrels burnt per day = 100 million

Global electricity production / year = 30,000 TWh

It is estimated by International Energy Authority that in 2025, 35% of the electricity produced will be from renewable sources.

In 2023, breakdown of renewable energy production according to the source is as follows: (Source: Statista.com)

Hydro	48 %
Wind	25 %
Solar	17 %
Other	10 %

The global daily production of electricity is over 82 TWh.

Conventionally electric power has to be used as it is produced. Demand for electricity changes with the time of the day. This requires that there should be a mechanism in place to match electricity generation and consumption.

A mechanism to store excess electricity produced during times of low demand and to make it available at times of high demand is therefore required. Pumped hydro, fly wheel, thermal storage, gas compression are some of the methods that have been developed.

Battery storage using electrochemical cells to store electrical energy has been used ever since the development of batteries over two centuries ago. Batteries that emerged as small scale power storage units have now reached a stage where they are employed in grid scale energy manipulation.

The role that has been played by the scientists and the chemists in particular, during this transformation is remarkable. Their dedication and hard work have immensely benefitted the people paving way for a comfortable life.

The global battery market is USD 104 billion today, and it is expected to grow with a compound annual growth rate (CAGR) of 15.8% from 2024 to 2031 reaching a market value of USD 201 billion. (Cognitive market Research, Battery market report, Global edition)

The Story of Battery Development

In 1800, the first battery consisting of electrochemical cells (voltaic pile) which could supply a continuous stream of electric current was invented by the Italian chemist Alessandro Volta. It consisted of alternating disks of zinc and copper with a cloth or paper separator soaked in a salt solution in between.

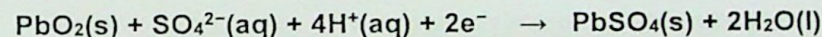
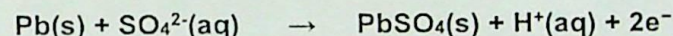
The other significant inventions that followed are,

1859	Gastea Plante (French) Lead/acid
1868	Geoges Leclanche (French) Zn / NH ₄ Cl
1899	Waldernar Jungner (Sweedish) NiCd
1900	Thomas Edison (USA) Fe/Ni
1969	Sealed lead acid and AGM
1971	Li primary battery
1989	NiMH

The lead acid battery which was invented in 1859 is a highly successful battery that is widely used as the starter battery in almost all the vehicles. Due to the presence of dilute sulphuric acid as the electrolyte, it has a very low internal resistance and it is ideal for obtaining large currents for short periods. However, deep discharge (> 30%) shortens the battery life.

Spirally wound, thin film lead acid batteries with high power outputs are now available.

The electrode reactions of the lead acid battery are:



Important features of this battery are:

- Catholyte and anolyte are the same (dil H₂SO₄)
- Separator is needed only to prevent physical contact of electrodes
- Electrode materials Pb, PbO₂, and PbSO₄ are insoluble in the electrolyte and this is crucial for the operation of the battery.

Single electrolyte makes the battery architecture simple. No ion-selective membranes are required.

Satisfying the condition (c) is quite tedious. Selecting a suitable electrolyte and proper electrode materials which are insoluble in the electrolyte, is extremely difficult.

Another feature that shows the cleverness of the inventor is its voltage (2.0V). This is a high value for an aqueous electrolyte considering water electrolysis above 1.2 V. However, the acid concentration is such that there is a substantially high discharge potential for gas evolution.

The invention of the battery (electrochemical cell) by Alessandro Volta triggered a cascade of other inventions and discoveries during the 19th century that led to rapid development of our understanding regarding the properties of matter.

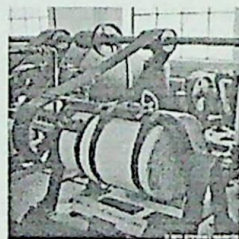
Experiments on electromagnetism by Joseph Henry (1830) and Michael Faraday (1831), Invention of electric motor by Moritz Jacobi (1834), and the investigation of the process of electrolysis by Michael Faraday (1831) and others are few such developments.

The concept of electric vehicles (EVs) is not new. It is as old as the invention of the batteries and the electric motor. Edison in 1900 was developing his Ni/Fe battery with the KOH electrolyte with the hope of using them in electric vehicles. Edison wanted his Ni/Fe battery to out-perform lead acid battery which was already available. By the time Edison was able to produce a powerful battery, his friend Henry Ford offered his gasoline powered vehicles at a lower cost. The market for EVs gradually waned in favor of gasoline powered vehicles. However, it is noteworthy that Thomas Edison's Ni/Fe battery pack had a range of 100 miles on a full charge.

Edison's Ni/Fe battery used Fe for its anode and NiO(OH) for the cathode. The electrolyte was KOH. It was similar to NiCd battery. As EVs became unpopular, these batteries were used in railway and in industry. Edison was an accomplished chemist, an engineer, a physicist and an inventor. He had a well-equipped chemistry laboratory and a very large workshop in New Jersey, USA.



Edison's Chemistry Laboratory



Ball mill

The Story of the Lithium ion Battery

Lithium ion battery technology stands out as a unique breakthrough in the history of the development of energy storage devices. It has excellent performance parameters as given below in comparison to other rechargeable batteries that were available at the time of its development.

Battery type	Voltage/V	Energy density (Wh/kg)	Cycle life
NiCd	1.2	60	2000
NiMH	1.2	120	1000
Lead Acid	2.0	50	1000
Li ⁺ ion	3.7	250	3000

In contrast to other re-chargeable batteries, Li ion battery operates through a process of reversible intercalation of Li⁺ ions between the electrodes. The electrolyte only provides a medium of transport for Li⁺ ions.

The story of the development of the Li⁺ ion battery, which dates back to 1972, amply illustrates the hurdles that scientists have to face and how they can be overcome through dedication and commitment.

In 1972, Stanley Wittingham, a young British chemist joined Exxon Research and Engineering in New Jersey, USA. Before long, he produced a battery with TiS₂ cathode and Li metal anode and a Li⁺ containing electrolyte. Its performance was unprecedented and much better than the best available rechargeable battery at that time.

It had a high power output and a voltage of 2.4 V. Initially the company (Exxon) showed some interest in the new battery. They manufactured coin cells that were used by a Swiss watch company for their solar powered wrist watch. However, the company soon lost interest in the TiS₂ battery and the production was discontinued.

Wittingham later said "I understood the rationale for doing it. The market just wasn't going to be big enough. Our invention was just too early". Exxon simply did not understand the potential of this invention. It was a bad start for Wittingham. (IEEE Spectrum), who really invented the rechargeable lithium battery. (Charles J Murray, 30, July 2023)

Wittingham had earned his PhD in Chemistry from the University of Oxford. John B. Goodenough who was also working at the University of Oxford was the next person to join the queue. A paper titled "Chemistry of intercalation compounds: Metal guests in chalcogenide

hosts" by Stanley Wittingham in 1978 made Goodenough realize that the future of battery research was with lithium.

Goodenough and one of his research students Koichi Mizushima commenced research work on lithium intercalation batteries. In 1980, they introduced Lithium cobalt oxide replacing titanium disulfide for the cathode. There was a remarkable improvement in the performance with the voltage escalating to 4V. The battery consisted of lithium metal foil as anode, LiCoO_2 as the anode and a lithium ion electrolyte.

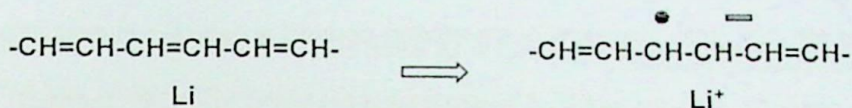
Goodenough wrote to many battery companies in the United Kingdom, USA and Europe with the intention of finding an investor to improve the product and to commercialize it. However, his efforts were in vain, no sponsors could be found. In desperation, he requested the University of Oxford to bear the cost of the patent. The request was declined. It was the general perception of the day that the commercialization of research outputs was not the business of a university.

Goodenough did not want to give up. Atomic Energy Research Establishment (AERE) is a government institution located near Oxford. He visited this institute and discussed the matter with them. They agreed to pay for the patent but on the condition that Goodenough writes away, his financial rights. He consented. AERE patented the invention in 1981. The inventors did not get any share of the initial battery earnings.

The next person to get involved in the development of the lithium ion battery was a young chemist by the name Akira Yoshino who was working for Asahi Chemical in Japan. Yoshino with a few other scientists, started experimenting with the newly discovered polyacetylene to ascertain if it could be used as an electrode material in batteries. In 1982, Yoshino came across a paper co-authored by Goodenough titled "Lithium ion batteries open the door to the future, hidden stories by the inventor" which described the use of LiC_6O_2 as a cathode material in lithium ion batteries. Yoshino and his team tried using polyacetylene as anode in a battery with LiC_6O_2 as the cathode.

Cis-Polyacetylene was the first conducting polymer that was discovered in early 1970's and its discovery opened up a fascinating new field of research with extensive applications. Hideki Shirakawa, Alan Heeger and Alan Mac Diarmid were awarded the Nobel Prize in Chemistry in 2000 for their contribution to the field of conductive polymers.

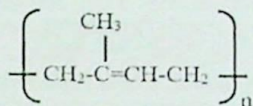
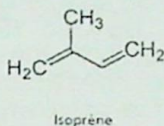
Polyacetylene interacts with Li transferring an electron to polyacetylene producing a radical anion (polaron) on the polymer. Such interactions enable polyacetylene to function as an anode material as well as to attain a high level of electrical conductivity



At this juncture I would like to take a few minutes to describe some related work that we have been doing at Peradeniya during the last few years.

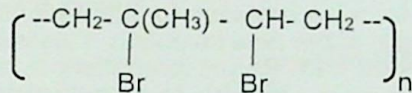
I begin with natural rubber. Why natural rubber? What does natural rubber have to do with Li ion battery? Natural rubber is *cis*-polyisoprene.

We recognized a unique structural feature in natural rubber molecule.

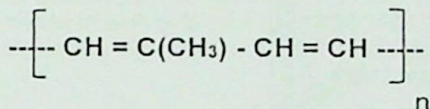


Natural rubber

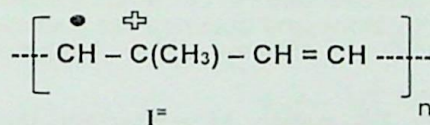
What happens if natural rubber is brominated and then dehydrobrominated?



Brominated NR



Dehydrobrominated product



Iodine doped product

The final product obtained after dehydrobromination was nothing but polyacetylene with a methyl substituent on every other C₂ unit. It is a conjugated polymer.

It is a conjugated polymer just like polyacetylene. We obtained it as a yellow product.

When doped with iodine (I₂), it turned almost black with a metallic lustre. Its electrical conductivity was in the metallic regime.

For the first time, we have been able to convert a natural polymer into a conducting polymer.

To continue with the work of Yoshino and his team at Asahi Chemical, they tested various carbon containing materials to be used as the anode. Finally, they decided to use petroleum coke. Goodenough was using metallic lithium for the anode. This was a potential safety hazard due to increased risk of fire. By choosing to use petroleum coke, Yoshino and his colleagues contributed to produce a very much safer battery.

Now Yoshino and his team had a crude prototype of the lithium ion battery. However, since Asahi was a chemical company, they did not have the equipment or the expertise to manufacture commercially acceptable batteries. With much effort the team was able to contact a small battery manufacturing company in Boston, USA. In 1986, two members of the research team at Asahi flew to Boston with the required chemicals to make a few hundred batteries. They returned to Japan with 200 of C type spirally wound cylindrical batteries. The company owners who manufactured the batteries were unaware of the fact that they manufactured the first lot of lithium ion batteries. However, Asahi chemical was reluctant to step into the commercial production of the battery.

One of the team members at Asahi, Kuribayashi visited the camcorder division of Sony Corporation in 1987 for a presentation to introduce the new battery. He took with him a sample of the new invention. This was the time when Sony was developing their own lithium ion battery to be used in the new camcorder that they were planning to manufacture. Sony was more than happy with the battery brought by the Asahi team. Sony engineers with their excellent facilities transformed the primitive prototype into a commercial product by 1989.

Finally, the Atomic Energy Research Establishment in UK which owned Goodenough's patent was contacted by Sony and obtained the license for the manufacture of the lithium ion battery which became commercially available since 1991.

It took two decades for Wittingham's TiS_2 battery to evolve into the modern version of the lithium ion battery. Currently Li^+ ion batteries use a mixture of transition metal oxides for the cathode. They are the oxides of Ni, Mn and Co (NMC) with the formula $Li(Ni_xMn_yCo_{1-x-y})O_2$. All these oxides have a layered structure.

runaway due to heating. In-between cathode compositions are non-stoichiometric and have higher conductivity.

Lithium ion technology is now well developed and there has been a ten-fold reduction in lithium prices during the last 10-12 years. The cost of Lithium ion battery packs is now below 150 USD/kWh and they are being used in MW scale grid balancing and energy storage applications.

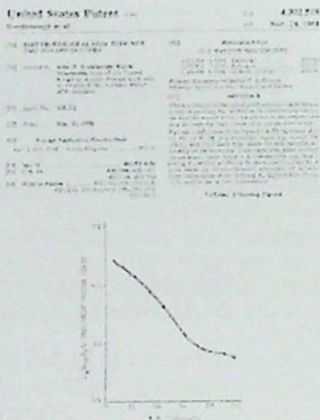


Fig. 4 Goodenough's patent

Voltage

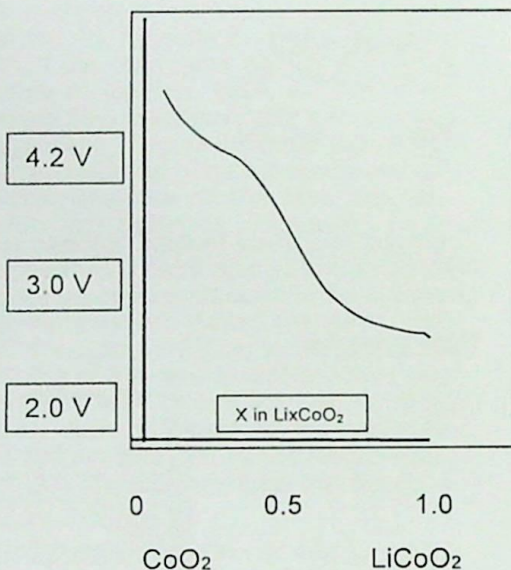


Fig. 5 charging curve

Charging beyond 4.2 V leads to delithiation, $x < 0.5$, leading to instability and induces phase change which can result in loss of capacity and cyclability.

Other Electrochemical Energy Storage Systems

- (a) Redox Flow Batteries
- (b) Supercapacitors

Redox Flow Batteries

These are medium to large scale stationary energy storage systems designed to store more energy than conventional batteries. They are rechargeable batteries and the technology was first developed during the early 19th century. Working flow batteries were demonstrated in electric vehicles in 1970's.

Essentially a flow battery consists of an electrode stack containing the electrochemical cells assembled in series through which the two electrolyte solutions, the anolyte and the catholyte, stored in two separate external tanks are circulated using electric pumps. Flow batteries have a larger capacity because more and more electroactive materials can be pumped through the stack during charging and discharging.

Although there are flow batteries with many different redox chemistries, there are two types which have reached technological maturity.

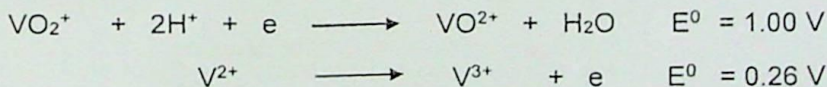
They are:

1. Vanadium flow battery
2. Zinc bromine flow battery.

Vanadium flow battery

Vanadium flow battery uses four different oxidation states of vanadium +II, +III, +IV and +V. The cell stack, like in any other flow battery, consists of a number of cells electrically connected in series. At the two ends of the stack are the end plates which are the current collecting terminals. Each of the other electrodes in the stack is a bipolar electrode as each is shared by two adjacent cells. The two electrolytes stored in two reservoirs are pumped through the stack using pumps. Electrolyte paths for each electrolyte supplying the stack are connected in parallel. In each cell there is a membrane separating the two electrolytes.

The electrode reactions are as follows



$$\text{Nominal cell voltage} = 1.26 \text{ V}$$

Forward reactions as shown above take place during discharge and the reverse reactions take place during charging. Graphite felt or carbon felt electrodes are used as metals corrode in the acidic solution. The two electrolytes in the cell are separated by an ion-selective membrane to prevent cross-over. The charged battery can be left for

long periods of time as the electroactive components are stored separately in tanks. The energy density of vanadium flow battery (VFB) is about 20-25 Wh/kg which is about ten times less than that of a Li⁺ ion battery. However, it is nonflammable and there is no capacity fading with time. Also, the VFB has a long cycle life of about 20,000.

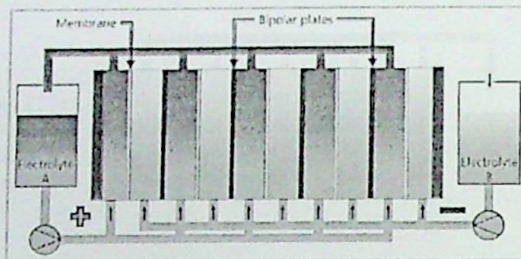


Fig. 6 Vanadium Flow Battery - Block Diagram

The largest VFB, with a capacity of 100 MW/400 MWh is now in operation in China.

Zinc – Bromine Flow Battery

The zinc bromide flow battery uses a 2 -2.5 M ZnBr₂ as the electrolyte. ZnBr₂ has a high solubility in water (450 g/100 ml at 20 °C). Carbon – plastic composite electrodes are used in the battery as metals cannot be used with the corrosive electrolyte, However, it has an energy density of about 60-85 Wh/kg which is higher than that of lead acid battery. The cell voltage is 1.78 V. It is capable of deep discharge (100%) with good reversibility.

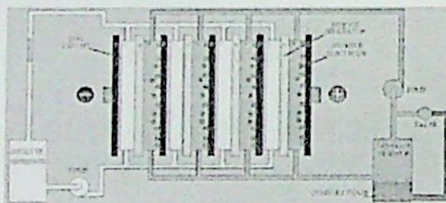


Fig. 7 Zn-bromine flow battery

(Andreas Poullikkas, in *Renewable and Sustainable Energy Reviews*, 2013)

The electrode reactions are as follows:



Cell voltage 1.76 V

During charging, metallic Zn is deposited on the cathode and Br_2 is formed in solution. It is therefore referred to as a hybrid flow battery. ZnBr_2 is regenerated during discharge.

High vapour pressure of bromine is a problem and usually a quaternary ammonium salt is added which binds with bromine forming a complex. Complex formation is reversible and bromine is released for reaction during discharge.

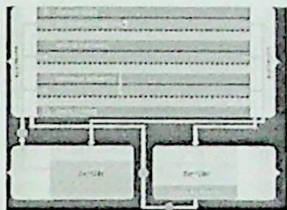


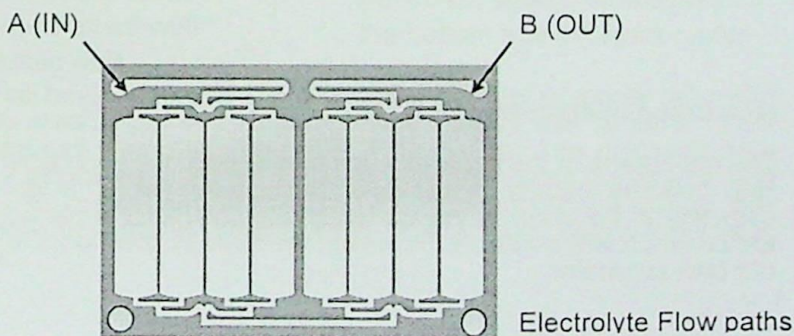
Fig.8 Flow battery with horizontal stack

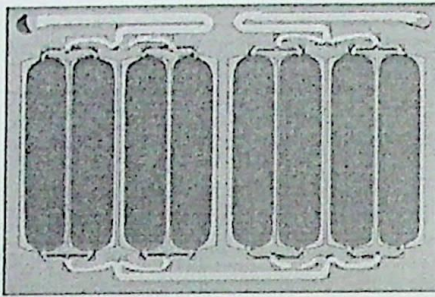
At Peradeniya, we have been working on zinc bromine flow battery for a few years. Our goal is to translate research findings into a useful product that will ultimately benefit the society. We always try to use local raw materials whenever possible. The ultimate objective is to develop a flow battery to store solar energy during day time and to utilize it during the night.

The battery stack, the heart of the battery, is a collection of electrodes mounted on flow frames, with separators in between. Microporous polymer membranes are used as separators. The two end-electrodes are the current collectors with terminal connections.

Electric Pumps are used to circulate the electrolytes through the stack. Flow balancing techniques are used to maintain equal pressures on either side of the membrane.

Flow paths on the flow frames are designed and optimized using flow simulation software.

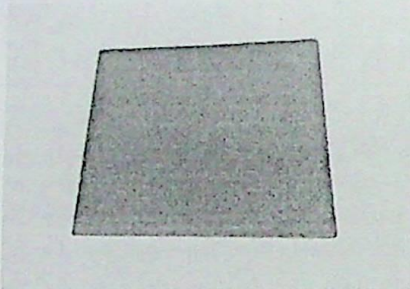




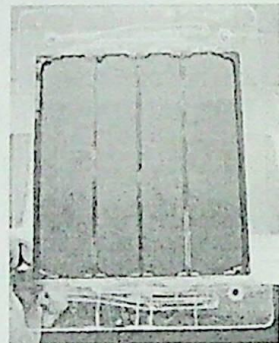
Flow simulations are used to ensure uniform flow of the electrolytes over the electrodes.

Electrodes:

Electrodes are manufactured by blending plastic materials with locally available graphite powder. Electrodes are then mounted on flow frames.



Electrode



Electrode mounted on flow frame showing the flow paths.

Membrane / Separator:

The membrane or the separator is a crucial part of a flow battery. In the zinc bromine battery, it prevents the cross-over of bromine from catholyte to the anolyte. We currently use polyolefin separators which are commercially available. However, we have initiated work to develop our own separator.



Prof. H. M. N. Bandara graduated from the University of Ceylon with a Bachelor of Science Honours in Chemistry degree in 1971 and was awarded the B. Z. F. Khan Gold Medal for best performance in the final examination. Soon after graduation, he joined the Peradeniya Campus of the then-University of Ceylon as an Assistant Lecturer in Chemistry and left for postgraduate studies in 1973. Prof. H. M. N. Bandara obtained his PhD in Inorganic Chemistry from the University of Aston, Birmingham, United Kingdom in 1977. On his return from the UK, he continued to serve at the Department of Chemistry, University of Peradeniya and was promoted to Senior Lecturer in 1982, Professor in Inorganic Chemistry in 1990 and Senior Professor in Inorganic Chemistry in 1999 in recognition of his contributions to the academic, administrative and research activities at the University. Further, he served as the Head of the Department of Statistics and Computer Science from 2006 - 2007 and subsequently as the Head of the Department of Chemistry from 2008 - 2011. He retired from the university service in 2013. Since 2000, Prof. H. M. N. Bandara contributed to national examinations, such as the G.C.E. (A/L) Chemistry examination, and served as the Controlling Examiner from 2006 - 2010. He was a distinguished visiting Professor at the Research Institute of Electronics, Shizuoka University, Japan from 2010-2011. Prof. H. M. N. Bandara is a research-focused person with over one hundred scholarly publications in international refereed journals. Due to his research interest, Prof. H.M.N. Bandara has been continuing research activities in the area of energy storage devices at the Department of Chemistry, University of Peradeniya, even after retirement and contributing towards institutional as well as national development.