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Investigation on Storage Technologies for Intermittent Renewable Energies: Evaluation and recommended R&D strategy

INVESTIRE-NETWORK

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WPST9-Metal-air systems

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1 Overview of the Storage Technology

Metal-air energy-storage systems utilise the electrochemical coupling of a reactive metal anode to an air electrode to provide a battery with an inexhaustible cathode reactant from the oxygen in atmospheric air. Metal-air batteries are characterised by high volumetric (kJ/m^3) and gravimetric (kJ/kg) energy densities and find typical applications as stand-alone power supplies (e.g. for stand-by or emergency power) or as clean power sources for transportation use. The overall capacity of such systems is determined by the ampere-hour capacity of the anode, and the means for handling and storing the metal oxide reaction product. A great deal of effort has therefore gone into the development of metal-air batteries for both power generation and energy storage over the last 25 years.

Various types of metal-air battery have been successfully developed, including zinc-air, aluminium-air, magnesium-air, iron(Fe^{2+})-air and lithium-air configurations, all operating in alkaline or neutral aqueous electrolytes. Both mechanically rechargeable and electrically rechargeable designs have been explored and developed, with varying success. In the former type, the discharged metal electrode is periodically replaced with fresh metal fuel, along with fresh electrolyte, and thus operates as a primary electrochemical cell. The air electrode is "unifunctional", acting only for the purpose of oxygen-reduction, and the battery works in discharge mode only. Electrically rechargeable metal-air batteries require the use of "bifunctional" air-electrodes, capable of both oxygen reduction (in discharge mode) and oxygen evolution (in charge mode). The development of reliable and efficient bifunctional air electrodes is still largely a matter for further research and may be key to the widespread application of metal-air systems for transportation use.

The main advantages normally associated with metal-air batteries include (Ref. 1):

- High energy density (compared to lead-acid batteries)
- Flat discharge voltage
- Long shelf life (dry storage)
- No major ecological problems
- Relatively low cost (on basis of metal used)

- Capacity independent of load and temperature when working within normal operating range.

Some disadvantages are:

- Not completely independent of environmental conditions (drying-out limits shelf life once exposed to air; flooding may limit power output)
- Limited power output
- Limited operating temperature range
- Hydrogen evolution from anode corrosion
- Carbonation of alkali electrolyte

Of all the metal-air batteries developed to date, zinc-air systems are the most highly developed, despite the fact that other metal electrode materials have higher theoretical energy densities and potentially better operating voltage characteristics (described later). The reasons why metal-air batteries (some texts refer to such systems as "fuel-cells") have not as yet found their way into common usage, apart from the small, high-capacity primary cells used in consumer electronics devices and hearing aids, is possibly due to the difficulties in developing efficient, practical fuel management systems, cheap and reliable bifunctional electrodes and the problems of setting up a fuel distribution infrastructure.

However as primary energy storage devices, metal-air, and particularly zinc-air, technology offers many advantages over competing systems such as lead-acid batteries, flywheels, hydrogen-storage for fuel cells, hydro-electric pumped-storage or gas-compression (strain energy devices). The future depends, as with all new technologies, on the developmental impetus given to innovative ideas and concepts.

1.1 Classification of Metal/Air cells based on active metal

Different active metals can be used as anode material. The type of the metal determines first of all the energy characteristics of the system.

Most investigated and used is the Zinc-Air system.

Aluminium-Air and Magnesium-Air Systems are also investigated.

Classification based on the electrolyte type

Water solutions of some acids, bases or salts are used as electrolyte in the metal-air cells.

1.2 Metal-Air Cells with alkaline electrolyte

Widely used in Metal-Air Cells are the alkaline electrolytes – water solutions of KOH or NaOH. They possess a high ionic conductivity and show comparatively a low corrosion activity in respect to some metals used as anodes in the metal-air systems. The use of alkaline electrolytes gives wider opportunity for the choice of different catalysts for the air electrode: carbon materials, silver, nickel, metal oxides etc.

1.3 Metal-Air Cells with neutral electrolyte

In some Metal-Air Cells water solutions of some salts: NaCl, NH4Cl, KCl, seawater etc. are used as electrolyte.

Actually these electrolytes are changing their pH value during the operation of the Metal-Air Cell because of generated OH – ions by the electrochemical reduction of the oxygen in the air electrode. This results in an increase of the pH (alkalization) of the electrolyte in the pores of the air electrode. It is more precise to say that the electrolyte is such cases is quasi-neutral.

1.4 Metal-Air Cells with acid electrolyte

Acid electrolytes are rarely used in Metal-Air Cells because they possess high corrosion activity both for the anode and cathode materials. The catalysts for such cells should be very stable in acid solutions, which narrows the range of their choice.

1.5 Classification based on the principle of operation

Beside the classical classification:

- primary metal-air cells
- secondary metal-air cells (metal-air accumulators)

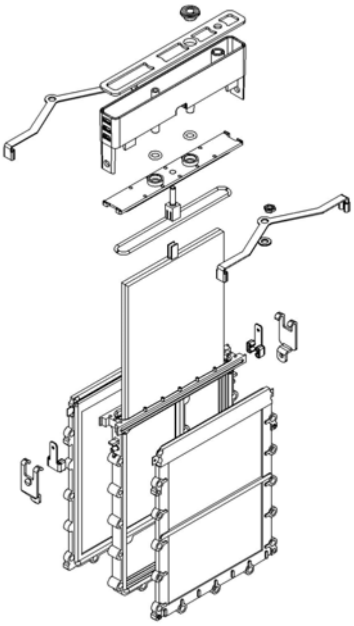
there exist also:

- mechanically rechargeable metal-air cells (the discharged metal electrode is taken out of the cell and is substituted with a charged one; the discharged electrode is charged or recycled outside the cell)

2 Technical characteristics and applications

2.1 *Components and materials of the technology*

Mechanical design: The actual design according to the ZOXY-system is shown in the explosion drawing for Metal/Air-systems. The connectors of the cell are shown in the upper part to give an idea how to collect the current.



Explosion drawing of the 80e Zinc/Air (System ZOXY)

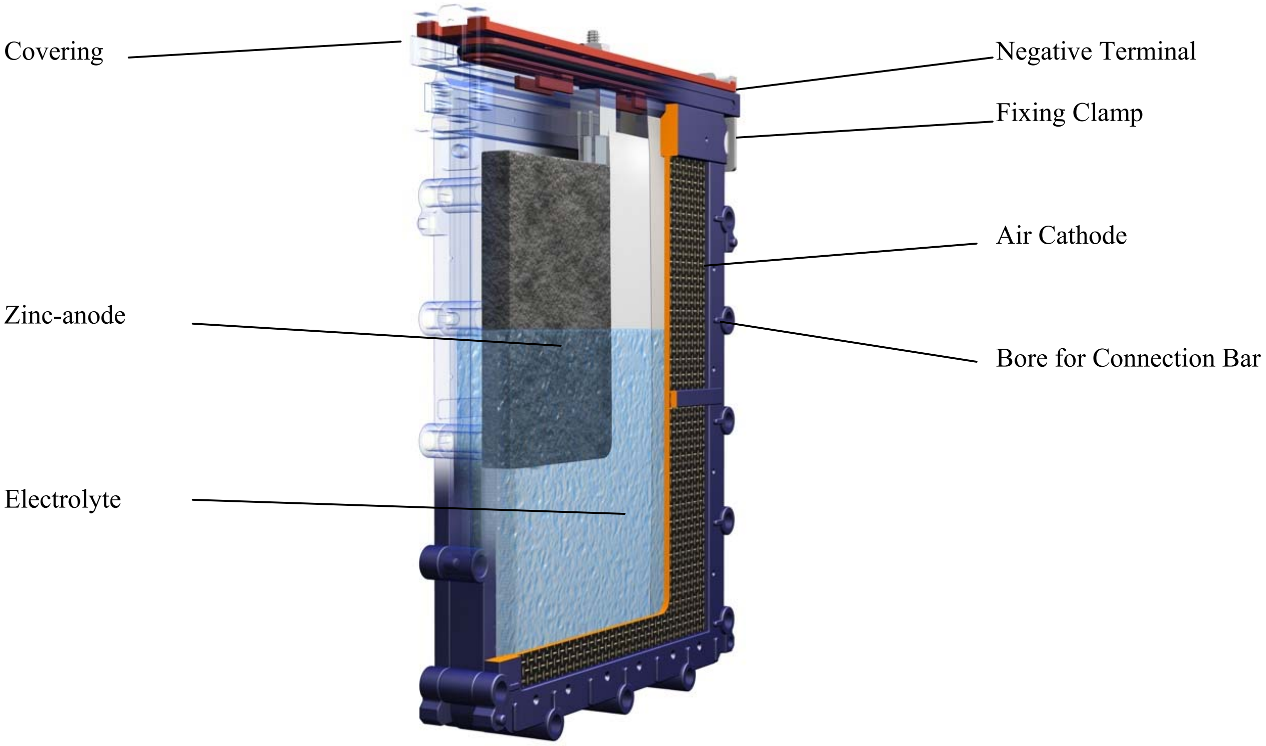
-Electrolyte reservoir

- Cover
- Connector

-Anode

- Casing and 2 cathodes

Description of the Zinc/Air-Cell 80e (system ZOXY)



The following electrode reactions represent the main reaction taking place in the

Zinc/Air-cell

Anode: $Zn + 2\ OH^{-} \longrightarrow ZnO + H_2O$

Cathode: $\frac{1}{2}\ O_2 + H_2O + 2\ e^{-} \rightarrow 2\ OH-$

Overall reaction: $Zn + \frac{1}{2}\ O_2 \rightarrow ZnO$

Due to the alkaline milieu the zinc-oxide ZnO is in equilibrium with the water soluble zincates $[Zn(OH)_4]^{2-}$ The formation of zincates are as follows:

$ZnO + H_2O + 2OH^{-} \quad [Zn(OH)_4]^{2-}$

Magnesium/Air-cell

Anode: $Mg + 2\ OH^{-} \rightarrow Mg(OH)_2 + 2\ e^{-}$

Cathode: $\frac{1}{2}\ O_2 + 2e^{-} + H_2O \rightarrow 2\ OH^{-}$

Overall reaction: $\frac{1}{2}\ O2 + Mg + H_2O \rightarrow Mg(OH)_2$

Aluminium/Air-cell

Anode : $2Al + 6\ OH^{-} \rightarrow 2\ Al(OH)_3 + 6e^{-}$

Cathode: $1{,}5\ O_2 + 6e^{-} + 3\ H_2O \rightarrow 6\ OH^{-}$

Overall reaction: $1{,}5\ O_2 + 2\ Al \quad 3\ H_2O \rightarrow 2\ Al(OH)_3$

2.2 Data and performance characteristics

2.2.1 System voltage

	Zinc/Air	Magnesium/Air	Aluminium/Air
Open circuit voltage	1,4 Volt/cell	3,08 Volt/cell	2,70 Volt/cell
Nominal voltage	1,0 Volt/cell	1,35 Volt/cell	1,2 Volt/cell
End-discharge voltage	0,8 Volt/cell		
	0,6 Volt/cell	0,6 Volt/cell	0,6 Volt/cell
Electrolyte	6M KOH	4M NaCl	4M NaCl

2.2.2 Range of capacities at several discharge rates and temperatures

Zn/Air 80e cell (ZOXY-system) at room temperature

70 % humidity, $C0_2$% (Air) < 30 ppm

Final discharging voltage: 0,8 Volt/cell

Discharging current	I/A	Capacity / Ah
C_{100}	1,0	100
C_{20}	4,5	90
C_{10}	8,0	80
C_5	11,0	55
C_1	25,0	25

2.2.3 Energy and power density

System	Cell-type	Wh/kg	Wh/l	Cell-type	W/kg	W/l
Zinc/Air	all	200-300	250-300	80e	70	80
Mg/Air						
Al/Air	Port16	450	700			

2.2.4 Cycling service and lifetime

Metal/Air-systems are principally operating as solid fuel cells. Therefore the lifetime cannot be expressed in terms of cycles but in operating time. Since the cathodes are the limiting factor e.g. for Zn/Air-systems, the operating time of the Zn/Air-cells (ZOXY) lay in the range of 2000 up to 5000 h.

Within the Zn/Air-systems also rechargeable cells are developed (ZOXY-system), which show cycle-numbers of 300 for solar application (at 5-10% DOD).
During an average lifetime 35 kWh have passed the cell (80e, ZOXY)

2.2.5 Faradic and energy efficiency

System	Faradic efficiency	Energy efficiency
Zn/Air	85%	ca. 50%

2.2.6 Self-discharge.

Zn/Air (ZOXY-System)

Open circuit
Environment conditions: 70 % humidity, $C0_2$% (Air) < 30 ppm
2%/week at room-temperature (activated)

2.2.7 Temperature

System	Operating Temperature range	Electrolyte
Zn/Air	-20 ^{0}C up to +60 ^{0}C	6M KOH

Mg/Air	-20 ^{0}C up to +60 ^{0}C	4M NaCl
Al/Air	-20 ^{0}C up to +60 ^{0}C	4M NaCl

2.2.8 Possible degradations during operation

Type of operation	Possible degradations within Zn/Air-cells
Overcharge	water dissociation causes only water loss, which can be compensated by service or a reservoir
deep discharge	formation of a too big non electrical conductive ZnO-phase, which cannot be recharged reversibly
cycling	geometrical changes due to vertical movements of ZnO-particles formation of Zn-dendrites

2.2.9 Recommended practices

Zinc/Air:

Only non-activated Zn/Air-cells should be transported.

The cell (ZOXY-systems) are always delivered charged and dry

The installation includes an activation step in which the cells are filled with KOH.

Electrical Recharging

The cells should be recharged with a constant current of 2.5 A, that corresponds to an average voltage of 1.9 V to 2,2 Volt per cell.

Recharging times equals discharging time multiplied by the overload-factor of 1.3.

There is no memory-effect, thus no reduction of capacity after short-time discharging and recharging.

Optimisation of the electrical performances

The electrical performance is mainly determined by the properties of the cathode. That means, that a higher surface enables the system to deliver higher currents for the application or that active ventilation results in a higher oxygen-reaction rate at the cathode.

2.3 Present situation of the storage technology

2.3.1 Technology developers and manufacturers

Main actors Metal/Air	**country**	**fields of applications**
AER Energy Ressources Inc .	USA	cellular phones, laptops
Electric Fuel Ltd,	Israel	electrical vehicles
Metallic Power Inc.,	USA	fuel-cell-mode
Powercell Corp.,	USA	power blocks
Zinc Air Power Corp.,	USA	electroscooters
Evonyx,	USA	fuel-cell-mode
Zoxy Energy Systems AG	BRD	USV, RAPS, fuel-cell-mode

RAPS = Remote Area Power Supply

Since the build up of markets is actually in charge it is not possible to define market shares

2.3.2 Constructional features and manufacturing methods

For metal/air-systems the active surface of the anode is of significant importance. In case of the zinc/air-system e.g. it is not possible to use a normal zinc-bulk-phase. Because of the lack in porosity it would not be possible to achieve higher currents. Thus a special technology of producing a zinc-sponge by electrochemical means can result into a condensed but porous metal-anode.

Because of the nature of the air-cathode, only prismatic designs are to favour for industrial applications, because definite voltages can be achieved by combining cells in a row.

2.3.3 Main conventional applications

Main applications for Metal/Air-systems

	Metal/Air-System		
Fields	**Zn/Air**	**Mg/Air**	**Al/Air**
Mobile Appl.	cellular phones	-	-
	laptops	-	-
Traction	wheel chairs	-	-
	electrical vehicles	-	-
	cleaning machines	-	-
Stationary	power blocks	power blocks	power blocks
	USV	-	-
	RAPS	RAPS	RAPS
Military	pilot phase of a variety of confidential applications		
fuel-cells	mechanical recharge mode	mechanical recharge mode	
starter	only possible as hybrid with a high energy storage source like supercapacitors		

Zinc-air batteries have traditionally been used as emergency or standby power sources in isolated locations. Apart from small button cells used widely in the electronics industry (mainly for hearing aids), larger industrial zinc-air batteries are only recently finding a new market as clean power sources for electric vehicles (EVs, scooters, cars, city buses and utility vehicles). At present mechanically rechargeable zinc-air systems and rechargeable systems have been developed. The prospects of the rechargeable Zn/Air-cells are good, with great progress being made in the materials sciences, especially for new catalyst compounds.

The major drawback with all metal-air systems is the relatively low current density obtainable, especially for the high currents demanded by electric vehicles. Rechargeable lithium-ion batteries are probably the frontline contenders, although such systems are expensive and present toxic hazards in the event of fire. Zinc-air systems are however based on relatively well-developed low-cost technologies. The main limitations to further rapid progress are undoubtedly in the design and development of the air electrodes, where a substantial improvement in achievable power density is required.

Rechargeable zinc-air batteries can be used for a wide range of energy storage applications in the general area of renewable energy electricity generation. Photovoltaic solar cells and other DC electricity generators (e.g. wind-turbines, wave power generators) produce relatively low voltage DC which can be fed directly into the battery. As the limiting capacity of stored energy depends directly on the amount of zinc present in a given battery, the high energy density of Zn-air systems offers large advantages for both PV roofing systems and power units for EVs.

2.3.4 Present R&D actions

Zn/Air: - cell for high cycles uses
- solid or fixed electrolyte
- kW power modules with high energy densities

Mg/Air - fast mechanical rechargeable cell

Al/Air - fast mechanical rechargeable cell

Present R&D actions are related to the ongoing search for better means for achieving improved power and energy densities, increased reliability and reduced costs. This research will undoubtedly lead to more compact metal-air systems for energy storage and generation for a wider range of application areas. Attention is clearly focusing on the development of new catalysts, improved electrode kinetics, and the use of new materials, particularly high-surface-area high porosity media for electrodes.

3 Economical issues

3.1 Cost of the storage technology

Cost versus storage capacity €/kWh

System	Price	Conditions	
Zinc/Air (ZOXY)	200 €/kWh	for smaller series	(10.000 12Volt-blocks/a)
	<50 €/kWh	for bigger series	

From a theoretical standpoint, the energy density of hydrogen is the highest of all common fuels. However, when engineering considerations are taken into account, such as the weight of the storage vessel, the theoretical value is reduced to 10% or less of its ideal value for a pure gas. Hydrocarbon fuels also have a high energy density (about 45000 kJ/kg, or 40000 MJ/m^3). On a volumetric basis, aluminium powder is comparable to hydrocarbons such as petrol, moreover it presents little or no risk from fire or explosion hazards, and is easily contained in low-mass storage vessels. Zinc is about one third as good as aluminium, but has the added advantage that the consumed product (zinc oxide) can be readily reconverted back to a pure metal. Aluminium-air batteries hold at least double the energy density of an equivalent lead-acid battery, and potentially as much as 4 or 5 times in a well-engineered system. The case for considering the electropositive metals such as zinc or aluminium as clean energy-dense storage media is therefore overwhelming.

Taking the electric vehicle market as typical for renewable energy systems in general, the US Advanced Battery Consortium has set targets for advanced battery development for the mid-term and long-term. In the mid-term, a specific energy density of 100 Wh/kg (at the C/3 discharge rate), and 200 Wh/kg in the long-term. Mid-term volumetric energy density is set at 135 Wh/litre (C/3 discharge rate), and 300 Wh/litre in the long-term.

Likewise, specific power targets are set at 200 W/kg (80% DOD/30 s) in the mid-term, 400 W/kg long-term, and volumetric power density targets of 250 W/litre (mid-term) and 600 W/litre (long-term). Target cost are given as <€150/kWh (mid-term) and <€100/kWh (mid-term) for mobile EV applications.

3.2 Installation, operating and maintenance cost

Evaluation of the cost of the total energy throughput during the estimated lifetime

Figures are not available yet, because a running field test has not been completed.

4 Environmental Issues

4.1 Current knowledge on environmental issues of the storage technology

Dangerous materials inputs:

Zn/Air:	no harmful materials used
Mg/Air:	no harmful materials used
Al/Air:	no harmful materials used

Emissions and safety aspects during manufacturing and operation:

	Safety aspects	Emissions
Zn/Air:	KOH handling	no
Mg/Air:	no	no
Al/Air:	no	only at Al-production

Disposal aspects

	Disposal of the product
Zn/Air:	via solarthermic process Via electrochemical process
Mg/Air:	can be applied to the normal Mg-production process
Al/Air:	can be applied to the normal Al-production process

4.2 Improvement options

One of the main advantages of Metal/Air-systems is their environmental profile, which includes the absence of any harmful material during all production and operation processes even today. Thus improvements of the environmental profile will be no topic.

5 Application of the storage technology for RES

5.1 Existing applications

A) Solarthermic Reduction of ZnO

I reduction with methane: $CH_4 + ZnO \longrightarrow Zn + CO + 2\,H_2$

II reduction with carbon: $2\,C + ZnO \longrightarrow Zn + 2CO$

III solarthermic dissociation: $ZnO \longrightarrow Zn + \frac{1}{2}\,O_2$

B) Direct connection of Zn/Air-cells to a solar panel
Special charger required (Zoxy system)

5.2 Operating characteristics

5.3 Assessment of the storage technology in these applications

5.4 *Potential future applications*

For point 5.2 – 5.4 the a.m. application A) is a focus of an actual EU-project “Solzinc”
(Solar Carbothermic Production of Zn of ZnO, Contract No. ENK6-CT2001-00512),
In which most of these aspects will be determined in 2003.
Electrochemical systems are inherently more efficient than other "internal combustion" devices such as heat engines, due to the intrinsic reversibility of many of the chemical reactions involved. Zinc-air systems are therefore well placed to take a good share of the future market for renewable energy storage.

Future potential applications of zinc-air battery technology may include integration with PV solar cell modules. This could be as separate storage devices for DC power much as lead-acid batteries are being used today. The development of reliable and cheap bifunctional air electrodes is key to their future success. Another possible development is the integration of specific PV material such as crystalline silicon directly with an "electron storage" material such as zinc, in a combined PV electricity generator-storage cell. This proposal envisages depositing a layer of metallic zinc directly onto the rear face of the silicon PV junction. The zinc layer would also be in contact with an electrolyte (gel), itself in contact with an air electrode forming the inside surface of the structure. Electrons passing across the junction from incident photons can be utilised to recharge zinc oxide back to zinc, and the PV energy incident on the solar panel could be immediately stored in the integrated zinc-air battery. Current for external use would be taken not from the PV's n-type and p-type junctions but from the zinc and air electrodes, as in a conventional zinc-air battery. Such a configuration would permit a large surface area zinc electrode to be deposited directly onto the silicon (or some other suitable material) wafer and gives an optimal distribution of electrons over the surface of the zinc at the electrochemical reaction sites.

6 Needs for R&D for an extended use in RES

One focus of actual R&D activities is the development of special Metal/air-chargers.
The main sources of renewable energy for electricity generation currently under development include photovoltaic solar cells, wind-turbines, wave power generators, underwater turbogenerators, hydroelectric and tidal barrage schemes, biomass and "energy from waste"

methane burners. Electrochemical systems can also be added to this list as part of a larger "green fuel infrastructure".

In all these RE systems, energy storage plays a dominant role where the energy cannot be utilised immediately. As all energy is simply work in transition, it can be converted into many forms before being stored in its final form. Pumped storage makes use of gravitational potential energy, but the possibilities for finding new sites is rather limited and is not without environmental consequences. Compressed gas schemes are likewise stored strain energy systems, but generally of limited capacity. Flywheels and other inertial systems are obviously kinetic energy stores. Nature generally opts for chemical energy as a means for long-term energy storage. In these respects, electrochemical systems are reversible chemical stores, and the centrifugal battery or fuel cell also combines chemical and kinetic energy storage options.

For solar, wind and other renewable energy sources, battery storage has many advantages where the energy supply is intermittent. Stored energy can be used when needed when the primary source is not available. For photovoltaic systems, typical applications include village power, telemetry, telecommunications, remote homes, lighting and other services. Important design considerations include high energy efficiency, low self-discharge, low cost, long cycle and calendar life, and little or no maintenance. System storage capacity varies from 0.05 - 1000 kWh with a voltage of typically 6 - 250 V DC. Battery capacity in the range 30-2000 Ah are needed at a charge rate of C/15 to C/500 utilising charge regulation methods. Discharge rates are typically C/5 to C/300, with an average daily depth-of-discharge of 1-30%, depending on battery type. Working temperature range of such PV battery systems is dependent on geographical location, and may vary between -40 - 60^{o}C. An average battery life of about 4 years is typical for low capacity (<350 Ah) cells, and 7-10 years for larger (>350 Ah) battery systems. Average costs are currently in the range 60-100 €100/kWh for lead-acid batteries.

No information is available at present for zinc-air photovoltaic systems, and demonstration projects are urgently needed involving manufacturers and R&D bodies to assess the future potential of such RE systems under realistic working conditions.

7 Conclusion and Recommendations

As a mean for the storage of electricity generated from renewable energy sources, zinc-air batteries hold out great promise in terms of their intrinsic specific energy density, certainly better than comparable lead-acid batteries by a factor of at least 4. However, their future usefulness in the extended field of renewable energy storage depends largely on the successful development of bifunctional air electrodes. The successful development of such electrodes, which is linked crucially with advances in material science and catalyst technologies, will open up many new markets in both stationary RE-derived electricity sources (PVs, wind-turbines, wave generators etc.) as well as in mobile power units for consumer electronics and electric vehicles.

The market for primary zinc-air batteries (with mechanically-rechargeable fuel electrodes) is growing, especially for EVs, but this market is competing with alternative power systems such as hydrogen-air fuel cells. Another approach for Metal-fuelled electrochemical systems is the continuous fuel supply. Both concepts have to be realised with new design concepts. The success of all such systems and eventual public acceptability will depend on many factors, not only economic but environmental, ease of use, establishment of a viable fuel infrastructure, safety and reliability. Metal-air systems are inherently safer than hydrogen-powered systems, but it must be demonstrated that the basic measures of specific energy and specific power achievable in practical systems are comparable or better than hydrogen-fuelled fuel cells.

Lithium-ion batteries are currently enjoying a very active development stage with demonstrable successes in both small-scale consumer electronics and large EV applications. Large capacity metal-air systems as such are less advanced, but do not suffer from the same environmental problems, make use of a "free" reactant source from atmospheric oxygen, and have the potential for possibly the highest energy densities. Rechargeable zinc-air systems can play a major role in these developments but more demonstration projects are needed to enable a better technical and economic assessment to be made.

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