

Solid State Energy Storage

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ABSTRACT

All solid state batteries (ASSB) have been researched by many groups in order to realize safe and high energy density rechargeable batteries. There are mainly two types of inorganic electrolytes used for ASSB: sulfides and oxides. We will review the recent advances in ASSB with oxide electrolytes. At first, the status of solid electrolytes will be discussed from the viewpoints of Li⁺ conductivity, chemical and electrochemical stability and compatibility with Li metal anode. In practical, the garnet electrolyte Li₇La₃Zr₂O₁₂ (LLZO), widely regarded as the most promising solid electrolyte, will be focused. Second, since it is very difficult to attach electrode layers to a LLZO pellet due to its surface nature, some deposition techniques, e.g., chemical vapor deposition (CVD) and physical vapor deposition (PVD), are used for electrode fabrication. Here, a new aerosol deposition (AD) technique to deposit cathode layer onto LLZO electrolyte is introduced. In addition, the wettability between LLZO and the most promising anode material, Li metal, is discussed. Finally, we would like to discuss the internal short circuit problem of ASSB due to Li metal penetration through LLZO pellet during charge and discharge processes. The understanding of this phenomenon is very important to realize practical all- solid-state batteries.

Keyword: - LLZO, Material, ASSB, Solid etc.

1. INTRODUCTION

A battery consists of two or more electric cells joined together. The cells convert chemical energy to electrical energy. The cells consist of positive and negative electrodes joined by an electrolyte. It is the chemical reaction between the electrodes and the electrolyte which generates DC electricity. In the case of secondary or rechargeable batteries, the chemical reaction can be reversed by reversing the current and the battery returned to a charged state. The 'lead acid' battery is the most well known rechargeable type, but there are others. The first electric vehicle using rechargeable batteries preceded the invention of the rechargeable lead acid by quarter of a century, and there are a very large number of materials and electrolytes that can be combined to form a battery. However, only a relatively small number of combinations have been developed as commercial rechargeable electric batteries suitable for use in vehicles. At present these include lead acid, nickel iron, nickel cadmium, nickel metal hydride, lithium polymer and lithium iron, sodium sulphur and sodium metal chloride. In this lecture the different types of the energy storage devices are presented. The following topics are covered in this lecture:

- Overview of Batteries
- Battery Parameters
- Lead acid batteries
- Lithium ion batteries
- Metal air batteries
- Battery Charging

From the electric vehicle designer's point of view the battery can be treated as a 'black box' which has a range of performance criteria. These criteria will include:

- specific energy
- energy density
- specific power
- typical voltages
- amp hour efficiency

- energy efficiency
- commercial availability
- cost, operating temperatures
- self-discharge rates
- number of life cycles
- recharge rates

The designer also needs to understand how energy availability varies with regard to:

- ambient temperature
- charge and discharge rates
- battery geometry
- optimum temperature
- charging methods
- cooling needs.

However, at least a basic understanding of the battery chemistry is very important, otherwise the performance and maintenance requirements of the different types, and most of the disappointments connected with battery use, such as their limited life, self- discharge, reduced efficiency at higher currents.

2. HISTORY OF THE BATTERY

Batteries provided the main source of electricity before the development of electric generators and electrical grids around the end of the 19th century. Successive improvements in battery technology facilitated major electrical advances, from early scientific studies to the rise of telegraphs and telephones, eventually leading to portable computers, mobile phones, electric cars, and many other electrical devices.

Scientists and engineers developed several commercially important types of battery. "Wet cells" were open containers that held liquid electrolyte and metallic electrodes. When the electrodes were completely consumed, the wet cell was renewed by replacing the electrodes and electrolyte. Open containers are unsuitable for mobile or portable use. Wet cells were used commercially in the telegraph and telephone systems. Early electric cars used semi- sealed wet cells.

One important classification for batteries is by their life cycle. "Primary" batteries can produce current as soon as assembled, but once the active elements are consumed, they cannot be electrically recharged. The development of the lead-acid battery and subsequent "secondary" or "rechargeable" types allowed energy to be restored to the cell, extending the life of permanently assembled cells. The introduction of nickel and lithium based batteries in the latter 20th century made the development of innumerable portable electronic devices feasible, from powerful flashlights to mobile phones. Very large stationary batteries find some applications in grid energy storage, helping to stabilize electric power distribution networks.

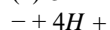
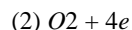


A voltaic pile, the first chemical battery

3. HYDROGEN FUEL CELLS: BASIC PRINCIPLES

Electrode reactions We have seen that the basic principle of the fuel cell is the release of energy following a chemical reaction between hydrogen and oxygen. The key difference between this and simply burning the gas is that the energy is released as an electric current, rather than heat. How is this electric current produced? To understand this we need to consider the separate reactions taking place at each electrode. These important details vary for different types of fuel cell, but if we start with a cell based on an acid electrolyte, we shall consider the simplest and the most common type.

At the anode of an acid electrolyte fuel cell the hydrogen gas ionizes, releasing electrons and creating H⁺ ions (or protons). $2H_2 \rightarrow 4H^+$



(3) Clearly, for both these reactions to proceed continuously, electrons produced at the anode must pass through an electrical circuit to the cathode. Also, H⁺ ions must pass through the electrolyte. An acid is a fluid with free H⁺ ions, and so serves this purpose very well. Certain polymers can also be made to contain mobile H⁺ ions.

4. DIFFERENT ELECTROLYTES

The reactions given above may seem simple enough, but they do not proceed rapidly in normal circumstances. Also, the fact that hydrogen has to be used as a fuel is a disadvantage. To solve these and other problems many different fuel cell types have been tried. The different types are usually distinguished by the electrolyte that is used, though there are always other important differences as well.

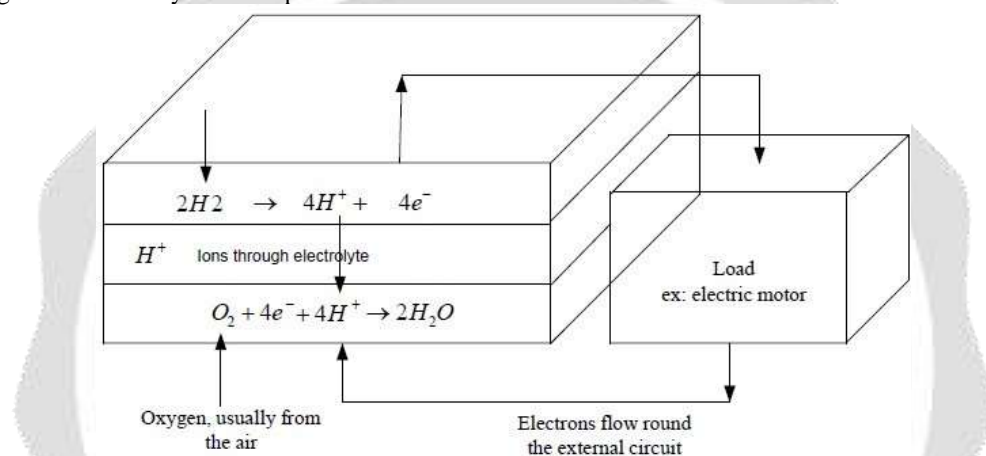


Table I: Data for different types of fuel cell

Fuel cell type	Mobile ion	Operating temp.	Applications and notes
Alkaline (AFC)	OH ⁻	50-200 C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H ⁺	30-100 C	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol(DMFC)	H ⁺	20-90 C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H ⁺	220 C	Large numbers of 200kW CHP systems in use
Molten carbonate (MCFC)	CO ₃ ²⁻	650 C	Suitable for medium to large scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O ²⁻	500-1000 C	Suitable for all sizes of CHP systems, 2 kW to multi MW

The situation now is that six classes of fuel cell have emerged as viable systems for the present and near future. Basic information about these systems is given in Table I. As well as facing up to different problems, the various fuel types also try to play to the strengths of fuel cells in different ways. The PEM fuel cell capitalizes on the essential simplicity of the fuel cell. The electrolyte is a solid polymer, in which protons are mobile. The chemistry is the same as the acid electrolyte fuel cell of Fig. 1. With a solid and immobile electrolyte, this type of cell is inherently simple; it is the type that shows by far the most promise for vehicles, and is the type used on all the most impressive demonstration fuel cell vehicles. This type of fuel cell is the main focus of this chapter. PEM fuel cells run at quite low temperatures, so the problem of slow reaction rates has to be addressed by using sophisticated catalysts and electrodes. Platinum is the catalyst, but developments in recent years mean that only minute amounts are used, and the cost of the platinum is a small part of the total price of a PEM fuel cell. One theoretically very attractive solution to the hydrogen supply problem

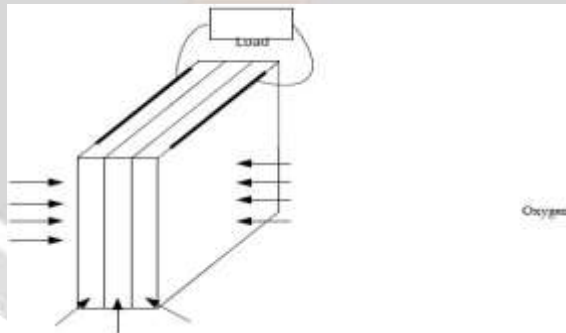
is to use methanol as a fuel instead. This can be done in the PEM fuel cell, and such cells are called direct methanol fuel cells. 'Direct' because they use the methanol as the fuel as it is, in liquid form, as opposed to extracting the hydrogen from the methanol using one of the methods. Unfortunately these cells have very low power, and for the foreseeable future at least their use will be restricted to applications requiring slow and steady generation of electricity over long periods. A demonstration DMFC powered go-kart has been built, but really the only likely application of this type of cell in the near future is in the rapidly growing area of portable electronics equipment. Although PEM fuel cells were used on the first manned spacecraft, the alkaline fuel cell was used on the Apollo and is used on the Shuttle Orbiter. The problem of slow reaction rate is overcome by using highly porous electrodes, with a platinum catalyst, and sometimes by operating at quite high pressures. Although some historically important alkaline fuel cells have operated at about 200°C, they more usually operate below 100°C. The alkaline fuel cell has been used by a few demonstration electric vehicles, always in hybrid systems with a battery. They can be made more cheaply than PEMFCs, but they are lower in power, and the electrolyte reacts with carbon dioxide in the air, which make terrestrial applications difficult.

Fuel cell electrodes

Fig. 2 is another representation of a fuel cell. Hydrogen is fed to one electrode, and oxygen, usually as air, to the other. A load is connected between the two electrodes, and current flows. However, in practice a fuel cell is far more complex than this. Normally the rate of reaction of both

hydrogen and oxygen is very slow, which results in a low current, and so a low power. The three main ways of dealing with the slow reaction rates are: the use of suitable catalysts on the electrode, raising the temperature, and increasing the electrode area. The first two can be applied to any chemical reaction. However, the third is special to fuel cells and is very important. If we take a reaction such as that of Eq. 3, we see that oxygen gas, and H⁺ ions from the electrolyte, and electrons from the circuit are needed, all three together. This 'coming together' must take place on the surface of the electrode. Clearly, the larger the electrode area, the more scope there is for this to happen and the greater the current. This is very important. Indeed, electrode area is such a vital issue that the performance of a fuel cell design is often quoted in terms of the current *per cm²*. The structure of the electrode is also important. It is made highly porous so that the real surface area is much greater than the normal length × width. As well as being of a large surface area, and highly porous, a fuel cell electrode must also be coated with a catalyst layer. In the case of the PEMFC this is platinum, which is highly expensive. The catalyst thus needs to be spread out as finely as possible. This is normally done by supporting very fine particles of the catalyst on carbon particles.

Fig. 2: Basic cathode-electrolyte-anode construction of a fuel cell



The reactants need to be brought into contact with the catalyst, and a good electrical contact needs to be made with the electrode surface. Also, in the case of the cathode, the product water needs to be removed. These tasks are performed by the 'gas diffusion layer', a porous and highly conductive material such as carbon felt or carbon paper, which is layered on the electrode surface.

5. ALTERNATIVE AND NOVEL ENERGY SOURCES

In addition to conventional electrical power sources for electric vehicles such as batteries and fuel cells, there is a range of alternative options including solar photovoltaics, wind-driven generators, flywheels and supercapacitors. There are also older systems which may be important in the development of electric vehicles, particularly electric supply rails either with mechanical pick-ups or modern ones with an inductive supply. In this lecture, considering stores of electrical energy, energy conversion devices, and energy transfer systems.

The following topics are covered in this lecture:

- Solar Photovoltaics
- Flywheels
- Supercapacitor Solar

Photovoltaics Photovoltaic cells are devices that convert sunlight or solar energy into direct current electricity. They are usually found as flat panels, and such panels are now a fairly common sight, on buildings and powering roadside equipment, to say nothing of being on calculators and similar electronic equipment. They can also come as thin films, which can be curved around a car body. Solar radiation strikes the upper atmosphere with a value of 1300Wm^{-2} but some of the radiation is lost in the atmosphere and by the time it reaches the Earth's surface it is less than 1000Wm^{-2} , normally called a 'standard sun'. Even in hot sunny climates solar radiation is normally less than this. Typical solar radiation on a flat plate constantly turned towards the sun will average around 750Wm^{-2} on a clear day in the tropics and around 500Wm^{-2} in more hazy climates. For a flat plate such as a solar panel placed on a car roof, the sun will strike the plate at differing angles as the sun moves around the sky, which halves the amount of energy falling on the plate. The exact average will depend on the latitude, being larger on the equator and less at higher latitudes. Solar radiation is split into direct radiation which comes from the direction of the sun which is normally prominent on cloudless days, and indirect radiation which is solar radiation broken up by cloud and dust, comes from all directions and is prominent on cloudy days.

6. CONCLUSION

All solid state battery has been developed by using sulfide solid electrolyte and now the cell can be fabricated. Within a few years, the all solid state battery with sulfide solid electrolyte may be commercialized. However, the sulfide solid electrolyte has some disadvantages, such as high sensitivity to moisture and release of H_2S toxic gas. Therefore, oxide solid electrolyte should be investigated. LLZO has some advantages, such as high stability to Li metal and relatively high Li^+ ion conductivity. Today, many researches have been started around the world. Unfortunately, we cannot precisely image the final design and materials for all solid state battery at this moment. But, there are many researches to clarify the interfacial and bulk phenomena taking place in all solid state battery. In future huge number of rechargeable batteries will be utilized to many applications, not only electric vehicle and smart grid, but also new portable applications. In such case, all solid state battery is suitable due to its extremely high durability, high safety and long cycle life.

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