

New and Old Types of Storage Batteries for Photovoltaics in Research and in College Curriculum

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Abstract

In the photovoltaics teaching curriculum the issue of need of energy storage is not central, but it is unavoidable corollary. Since in many storage applications, it is the electrochemical storage scheme that is employed, fundamental instruction about batteries is needed. From general principles of dissimilar materials and redox reactions one will make transition to various types of electrochemical systems. Knowledge of longevity and modes of failure of batteries became necessary part of complex knowledge needed to grasp the intricacies of energy economy.

Keywords: photovoltaics, education, instruction, batteries, electrochemical energy storage

ENERGY STORAGE AND PHOTOVOLTAICS

Needs to Teach about Energy Storage

For small and short term energy storage from photovoltaics can be a capacitor or a flywheel. For some specific, single-purpose systems, for example water pumping for refrigeration, the storage medium can be water or ice. However, in photovoltaics the most common type of storage by far is chemical storage in the form of battery.

Teaching Electrochemistry

Teaching about electrochemical batteries, either as a convenient energy source or specifically as a pawn in energy storage can take various approaches. With proliferation of technology the present pupils and students paradoxically have less exposure to the "bare" batteries, individual cells that could be explored. While batteries are omnipresent, they are often embedded in devices even without easy means of removal. Gone are the days when hobbyist used the flat 4.5-V battery (3LR12), which was with its metal pads so easy to use in projects.



Fig. 1. Classical 4.5-V dry battery, type 3LR12. The metal tabs were convenient connections for hobbyist projects.

The textbook Cu-Zn Daniell cell [1] is often discussed but hardly ever constructed. What remains is a lemon battery demonstration. Nevertheless, it is possible to introduce new and interesting experiments to the classrooms.

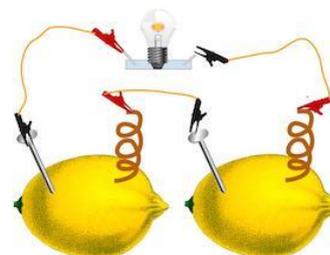


Fig. 2. Schematic drawing of the lemon battery often shown at school science fairs. The electrodes are zinc plated steel nail and copper in the copper conductor. Lemon juice is the electrolyte.

Those who in spite of prior exposure to chemistry and engineering enter the realm of electrochemical power sources research will enter exciting world of material science.

The Primary and Secondary Batteries

The described flat (3LR12) battery, the Daniel cell and even the lemon demonstration project are examples of the called primary batteries, a term used for systems that due to electrochemical reactions produce electrical energy, but once the chemicals are depleted, energy is no longer produced and the batteries cannot be in a simple manner restored to the original state. Therefore, by design these batteries are single use and have to be discarded after one use. While this can be at times convenient, more useful service comes from systems that can be, once discharged, connected to a source of electrical energy and recharged to the original state. These are the secondary batteries, often called rechargeable or storage batteries and in some use also accumulators.

Photovoltaics Can't be Done Overnight

Every student of photovoltaic will at some point come to the realization that a system, which relies on sunshine, will deliver energy only during daylight. For some it may be simply a matter of fact; those involved in complete energy solution will have to deal with the task to store some of the photovoltaic energy generated during daylight for use later on when it is dark. While not the only storage solution, energy storage using electrochemical principles is very convenient and often used.

TYPES OF STORAGE BATTERIES

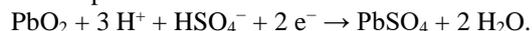
Lead-acid

This battery was invented already in 1859 by Gaston Planté [2]. It consists of two lead-based electrodes. The negative electrode is metallic lead; the positive electrode is porous mass of lead(IV) oxide. Each individual cell of the battery is filled with sulfuric acid and the cell, when charged, has nominally voltage of about 2.105 V.

The reaction during discharge on the negative electrode is



and on the positive electrode



Thus on the negative electrode the metallic lead is oxidized and turns into lead(II) sulfate, while lead(IV) oxide on the positive electrode is reduced and turns also to lead(II) sulfate. While these two reactions are happening, some of the sulfuric acid in the electrolyte is also consumed. Once the oxide in the battery is

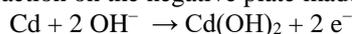
consumed, the system loses power, but it can be recharged from an outside source of electricity, by inverting the above reactions.

A basic type is so called battery with flooded electrodes - e.g., a car of classical design battery - where the electrolyte is a free liquid between electrodes. Newer design is so called VRLA type (Valve Regulated Lead Acid) which is an encapsulated type with a significant reduction of gas evolution; practically no oxygen evolves and only a very small amount of hydrogen is formed. They can be in the form of AGM (from Absorbent Glass Mat) which has the electrolyte soaked in the glass wool between electrodes and the gel form, where the electrolyte is thickened in the form of a gel.

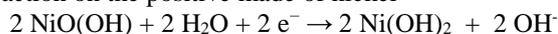
Nickel-Cadmium and Nickel-Iron

Cadmium was found as impurity in zinc production in 1817. It has similar properties to zinc and mercury, which is the reason why each three of these metals found use in electrochemical cells. Cadmium found its use in energy sector as the negative electrode of a rechargeable nickel-cadmium battery. The cells based on this chemistry were invented in 1899 by Waldemar Jungner [3] [4]. The chemical reactions are as follows:

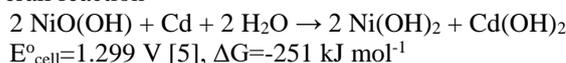
Reaction on the negative plate made of cadmium



Reaction on the positive made of nickel



Overall reaction

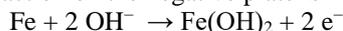


The electrolyte is usually 21% potassium hydroxide and the average operating voltage is 1.2 V.

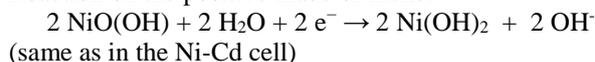
The second metal used in this setup is nickel, which has application in another rechargeable battery system, the nickel-iron secondary battery.

The nickel iron (Ni-Fe) battery is a storage battery quite tolerant and more so than a lead-acid battery to overcharge, deep discharge and short circuit and thus it has been popular in backup situations and in on-site industrial electric vehicles and forklifts. Just as the nickel-cadmium, the nickel-iron battery was invented in 1899 by W. Jungner [3], but the nickel-iron design was improved in 1901 by Thomas Edison. The battery uses alkaline electrolyte, sodium or potassium hydroxide. Open circuit voltage of the cell is 1.4 V, and drops during discharge to 1.2 V.

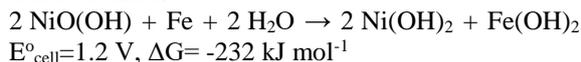
Reaction on the negative plate is



Reaction on the positive made of nickel



Overall reaction is



Nickel-plated or nickel based items are quite common, including some coins, though they are known in some individuals cause nickel allergy (e.g., in jewelry). Even though nickel is less problematic than cadmium, it is still considered toxic and is a category 3 carcinogen (in European Union classification, i.e., "Substances which cause concern for humans, owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment") so one category less severe than cadmium. Because of the nickel-cadmium combination of rechargeable batteries, nickel ends up to be suppressed as a material for electrochemical sources as well. Nickel finds its use in the Ni-Fe rechargeable batteries, which have low charge/discharge efficiency but are operational up to -40°C and excel in longevity from 30 up to perhaps 50 years [1]. Iron is not environmental hazard in these applications.

While Jungner invented the nickel-cadmium battery already in 1899 as a wet cell [3] sealed cells became very popular towards the later part of the twentieth century as portable electronics became more and more available. The Ni-Cd batteries are able to deliver high currents and thus they became very popular as a power for remote controlled models. The advantage was also that the batteries can operate at higher temperatures and they can also operate well below 0°C . The low temperature is somewhat an advantage over presently used (standard) lithium cells, which lose both capacity and ability to be charged by high currents unless electrolytes with particularly low viscosity at low temperature are employed.

Cadmium is, however, environmental pollutant, a category 2 carcinogen (in European Union classification, i.e. "Substances which should be regarded as if they are carcinogenic to humans.") and its use in batteries became in Europe heavily curtailed. The 2006 Battery Directive [6] restricted severely the use of cadmium batteries to be used only in emergency lighting, emergency doors and alarms systems, in medical equipment and in cordless power tools. In 2006 battery operated power tools were widespread and the Ni-Cd batteries were still the only viable alternative, so there were included in the exception. However, as lithium batteries became more available, the Battery Directive was amended and in 2013 the use of Ni-Cd in power tools was also banned. It should be also noted that through effort of individual countries the efficiency of recycling Ni-Cd systems (regardless of the 2013 ban in power tools) has increased significantly (Fig. 5).

Lithium

Lithium ion batteries are ubiquitous today, used in cell phones, laptops, and many other devices. Efficient battery development is also a key in allowing move away from fossil fuels, as the batteries enable storage of energy generated from solar, wind and other renewable sources.

The importance of the lithium cells and the world-wide impact of these devices were significantly acknowledged by the 2019 Nobel Prize in Chemistry that has been awarded to three electrochemists for the development of a rechargeable battery based on lithium. Stanley Whittingham developed the first functional lithium battery in the early 1970s, but it was possibly too explosive to be commercially acceptable. John B. Goodenough was responsible for developing far more powerful batteries. Akira Yoshino later eliminated pure lithium from the battery, using lithium ions only to shuttle between the cathode and anode, producing the first commercially viable lithium ion battery in 1985. This is safer than pure lithium and made the battery workable for real-world applications. While lithium batteries are undoubtedly most prominently on people's minds today, other chemistry schemes are finding their application as well.

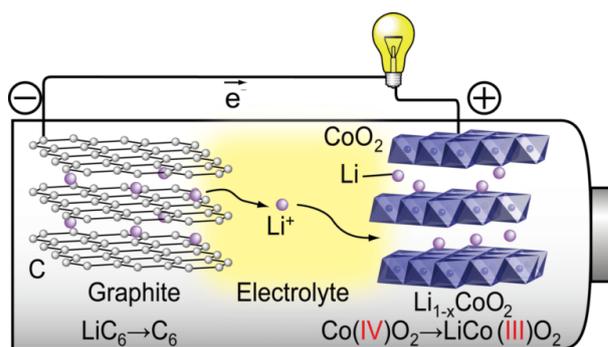


Fig. 3. A diagram of the modern type of lithium-ion based rechargeable battery.

Lithium-ion battery of the modern design is not based on reduction or oxidation processes. Instead, lithium cation is driven during charging and then during discharging between two materials that can efficiently incorporate and then release the ions. So the charging/discharging is moving the ions back and forth, a scheme sometimes referred to as "rocking chair." The negative electrode is a form of graphite, the positive electrode is, in the simplest form, cobalt(IV) oxide, that can incorporate lithium ion, rendering in the step cobalt formally trivalent [7].

Flow-Through Cells (RedOx)

The expression "redox" is derived from joining two words, reduction and oxidation, implying simultaneous occurrence of both of these processes, oxidation, loss of electrons and reduction, gain of electrons. From the general electrochemical point of view, where the overall

charge balance is thermodynamically required, any electrochemical system will be a "redox" system. However, in the vernacular of electrochemical power sources, the *redox flow battery* was adopted for a particular concept of electrochemical energy storage.



Fig. 4. An actual commercial vanadium flow cell. The left and right upper containers in the transport cages hold the respective vanadium solutions. The middle is the armature of the electrochemical cell. The containers and the cell are placed over the blue reservoirs intended to capture any spill in case of an accident. For sizing an Estwing 22, a 13" geological hammer, is leaning against the middle retention reservoir.

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A redox flow battery (often abbreviated RFB) describes a power source that uses for energy generation two separate solutions, one in an oxidized form, the other in a reduced form. During release of energy the solutions react on electrodes, the first is reduced and the other is oxidized and in the outside circuit between the two electrodes flows electric current. During the process of charging the function of oxidation and reduction is reversed and the system is charged from an external energy source.

The principle of the flow redox cells is the same as the principle of any galvanic cell. Oxidation and reduction, occurring simultaneously, but in separate half-cells, cause the flow of an electric current, carried by ion flow in the electrolyte of the electrochemical cell and by electrons in the external electric circuit. This electric current is then the source of energy carried by conductors to wherever it is needed. Compounds that undergo oxidation or reduction are sources of chemical energy. When these substances are reacted and spent, the electrochemical cell is discharged. For rechargeable (secondary) cells, the discharge process can be reversed

and the cell again recharged via an external power source. Reactive substances pass into their original form during charging. However, the redox flow cells differ from the conventional electrochemical cells by the fact that the reacting material is not part of the construction of the cell, but it is supplied from external storage tanks in a form of electrolytes which, during cycling, pass from the charged to the discharged state. The total energy capacity of the system is proportional to the amount of electrolytes in the external reservoirs, while the total output power is dependent on the electrode arrangement (the surface of the electrode system). In a sense, the behavior of the flow cell, when delivering energy, is identical to the fuel cell operating principle. However, the fuel cell is not expected to reverse the current flow and recharge the system again. The diagram of the redox flow cell, showing its principle, is given in Fig. 5.

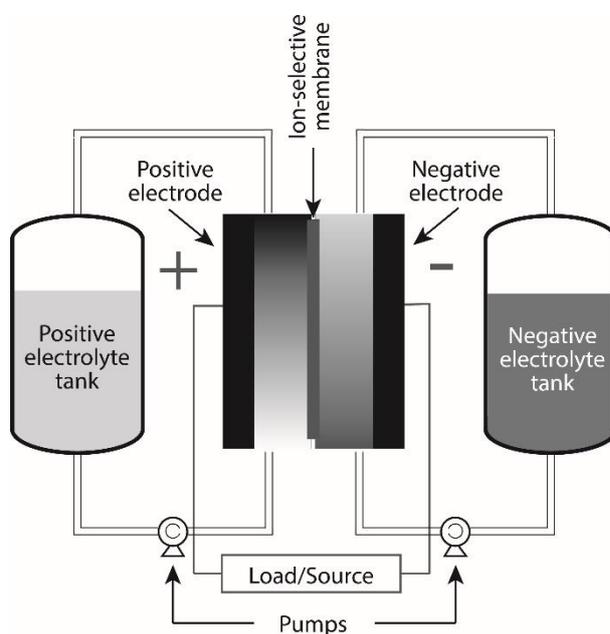


Fig. 5: Diagram of the principle of a redox flow-through cell.

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