



# Energy storage materials: A perspective

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## ARTICLE INFO

### Article history:

Received 25 July 2015

Accepted 25 July 2015

## ABSTRACT

Storage of electrical energy generated by variable and diffuse wind and solar energy at an acceptable cost would liberate modern society from its dependence for energy on the combustion of fossil fuels. This perspective attempts to project the extent to which electrochemical technologies can achieve this liberation. Realization of a reversible plating of a Lithium or Sodium anode through a solid  $\text{Li}^+$  or  $\text{Na}^+$  electrolyte would offer the best solution for a rechargeable battery that powers electric vehicles, thereby replacing the internal combustion engines that are creating a distributed emission of polluting gases from an increasing fleet of automobiles. Removal from the cathode to an external store of the product of the chemical reaction on discharge of a rechargeable battery can increase the capacity and lower the cost of stationary electrical energy storage in a battery. The ability to store electrical energy from wind and/or solar energy in rechargeable batteries at distributed sites can lower the cost and enhance the security of energy availability. The contributions from electrochemical capacitors and reversible fuel cells are also considered.

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## 1. The challenge

The need to liberate modern society from its dependence on fossil fuels is made urgent by the expanding human population, by global warming from the burning of fossil fuels, by the increasing cost of extraction and distribution of fossil fuels, and by an uneven distribution of finite fossil-fuel stores that continues to lead to conflict between and within nations. Alternative, practically inexhaustible energy sources exist: wind and/or solar energy are ubiquitous and can be converted locally into electrical energy, but they are diffuse and variable over diurnal and seasonal time scales; the electrical energy from these sources must be concentrated and stored for use on the diurnal and seasonal time scales of energy demand. Nature stores solar energy as hydropower and biomass; our challenge is to concentrate the electrical energy derived from solar and wind energy into both portable and stationary stored energy that is efficiently and rapidly convertible, without air pollution, back into electrical energy.

Energy is stored most conveniently as chemical energy; the fossil fuels represent the storage of solar energy as chemical energy over billion-year time scales. Fossil-fuel energy is converted into heat by combustion with attendant polluting gas emissions. Electrochemical technologies, on the other hand, offer the interconversion of electrical and chemical energy on a minute,

or shorter, time scale without polluting gas emissions and, at least theoretically, with greater efficiency than that of a heat engine. Today's challenge is the design of an electrochemical technology that can perform safely the task of electrical-energy storage and recovery at a rate and cost that are competitive with the performance of the well-established fossil-fuel technologies.

## 2. Rechargeable electrochemical technologies

An electrochemical cell consists of two electronically conducting electrodes, the *anode* and the *cathode* that are separated from each other by an *electrolyte*. In the charged state of a cell, chemical energy is stored as a *reductant* at the anode and an *oxidant* at the cathode. The function of the electrolyte, which is an electronic insulator and an ionic conductor, is to separate the electronic and ionic components of the chemical reaction between the reactants at the two electrodes; the electrolyte transports the ionic component inside the cell and forces the electronic component to traverse an external circuit. The ionic component of the reaction is called the *working ion*. On discharge, the cell delivers in the external circuit an electronic current  $I_{dis}$  at a voltage  $V_{dis}$ , i.e. electric power  $P_{dis} = I_{dis}V_{dis}$ , for the time  $\Delta t_{dis}$  to complete the chemical reaction. Electrical-energy storage in a cell requires a chemical reaction that is *reversible* on the application of a charging electric power  $P_{ch}V_{ch}$  that separates the two reactants of the

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<http://dx.doi.org/10.1016/j.ensm.2015.07.001>

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reversible chemical reaction back to the two electrodes. The product of the reaction is at the cathode if the electrolyte transports a cation; it is at the anode if the working ion is the oxide anion. The efficiency of electrical-energy storage is  $100 P_{dis}/P_{ch}\%$ .

Of particular interest for this perspective are three types of rechargeable electrochemical cells: batteries, fuel cells, and electrochemical capacitors. Individual cells may be connected in series and/or in parallel to obtain a total desired power  $P=IV$ . The critical components of these electrochemical technologies are those of the individual cell.

In the cells of a rechargeable battery, the reductant and the oxidant are normally solids with a liquid electrolyte or are molten solids with a solid electrolyte since ionic transport across a solid-liquid interface can be facile. Reversible reactions in a solid cathode occur where a working cation,  $\text{Li}^+$  or  $\text{Na}^+$ , can be inserted reversibly as a guest into a transition-metal compound host; the transition metal of the host provides the redox energy of the cathode. The  $\text{S}_8$  molecule is also a potential solid cathode. However, the cathode of a rechargeable cell may also be gaseous oxygen with catalytic electronic conductors for the oxygen-reduction and the oxygen-evolution reactions (ORR and OER) or a flow-through liquid containing a soluble redox molecule provided the separator is able to prevent the redox molecule from reaching the anode. At an air cathode, oxygen is obtained from the air on discharge and exhausted to the air on charge. The product of a liquid-cathode reaction may also be stored externally.

In the cells of an electrochemical capacitor, the reactants are electrons or electron holes trapped electrostatically by electrolyte cations or anions, respectively, across a double layer at an electrode-electrolyte interface. The discharge of an electrochemical capacitor can be much faster than that of a battery since ionic transfer is only within the electrolyte; but the storage capacity of a capacitor is generally much smaller since energy is stored only at the electrode surfaces and not in the bulk of the electrode.

In a reversible fuel cell, the electrolyte must transport an anion, not a cation, if it is to store electricity. For example, in a solid oxide fuel cell (SOFC), the electrolyte transports  $\text{O}^{2-}$  ions. On discharge, the fuel  $\text{H}_2$  is converted catalytically to  $2\text{H}^+ + 2\text{e}^-$  at the anode where the  $\text{H}^+$  ions react with the  $\text{O}^{2-}$  ions of the electrolyte to exhaust gaseous  $\text{H}_2\text{O}$  that can be stored externally in a chemical bed by oxidizing a metal, e.g.  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ , with the  $\text{H}_2$  returning to the anode to continue the discharge reaction. At the cathode,  $\text{O}^{2-}$  ions are restored to the electrolyte by the ORR,  $\text{O}_2 + 4\text{e}^- = 2\text{O}^{2-}$ , with the oxygen supplied by air. On charge, reversing the charge flow reverses the gas flow;  $\text{O}_2$  is returned to the air from the air cathode by the catalytic OER and  $\text{O}^{2-}$  is returned to the electrolyte at the anode in the reaction  $\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + \text{O}^{2-}$  with water obtained by reduction of the oxide bed, e.g.  $4\text{H}_2 + \text{Fe}_3\text{O}_4 = 3\text{Fe} + 4\text{H}_2\text{O}$ , with the return of  $\text{H}_2$  to the storage bed to continue its reduction until the storage bed is fully recharged. However, if the electrolyte of the fuel cell transports  $\text{H}^+$  ions,  $\text{H}_2\text{O}$  is produced at the cathode on discharge and the gas flows are not reversed on reversing the electron flow from  $P_{dis}$  to  $P_{ch}$ .

### 3. Useful relationships

At a fixed discharge current  $I_{dis} = dq/dt$ , the total volumetric or specific energy stored in a rechargeable cell of a battery or an electrochemical capacitor is

$$\Delta E = \int_0^{\Delta t_{dis}} P_{dis} dt = \int_0^{Q(I_{dis})} V(q)_{dis} dq = \langle V(q)_{dis} \rangle \cdot Q(I_{dis}) \quad (1)$$

where  $q$  is the state of charge of the cell,  $\Delta t_{dis}$  is the time at  $I_{dis}$  to complete a full chemical reaction and,

$$Q(I_{dis}) = \int_0^{\Delta t_{dis}} I_{dis} dt = \int_0^{Q(I_{dis})} dq \text{ per volume or weight} \quad (2)$$

is the volumetric or specific capacity of an electrode in a half-cell. Normally, a two-phase reaction occurs at the anode. In the reaction range of  $q$  where the chemical reaction at the cathode is two-phase,  $V(q)$  is constant; where a single-phase insertion reaction occurs,  $V(q)$  decreases with  $q$ .

The voltages  $V_{dis}$  and  $V_{ch}$  of a rechargeable battery cell change with the currents  $I_{dis}$  and  $I_{ch}$ . The changes  $\eta(I, q) = IR_b(q)$  are the result of the internal cell resistance  $R_b(q)$  to ion transfer inside the cell:

$$V_{dis} = V_{oc} - \eta(I_{dis}, q) \text{ and } V_{ch} = V_{oc} + \eta(I_{ch}, q) \quad (3)$$

where

$$eV_{oc} = \mu_A - \mu_C \quad (4)$$

The  $\mu_A$  and  $\mu_C$  are, respectively, the electrochemical potentials of the anode and cathode;  $e$  is the magnitude of the electronic charge, and  $V_{oc} = V(q)$  for  $I_{dis} = I_{ch} = 0$ . The  $\eta(I, q)$  are called the polarization on discharge, the overpotential on charge.

The coulomb efficiency of a battery-cell electrode in a half-cell or of a full cell is  $100\Delta t_{dis}(n+1)/\Delta t_{dis}(n)\%$ , where  $n+1$  and  $n$  refer to the number of charge/discharge cycles. The coulomb efficiency is a measure of cycle life; a cell is normally retired after the capacity is reduced to 80% of its original value. The capacity fade is generally largest in the first few cycles, so it is normally reported for larger values of  $n$ .

In an electrochemical capacitor, only the resistance to ionic transport in the electrolyte is present, and capacity fade on cycling need not be a problem.

In a cell with an air electrode, as in a fuel cell, the stabilities of the cathode catalysts for the ORR and/or OER are of concern; a long cycle life requires stable electrocatalysts.

### 4. Electrolyte constraints

From the above considerations, the electrolyte of a rechargeable electrochemical cell must provide not only a low internal resistance to the diffusion of the working ion in the electrolyte but also, except in an electrochemical capacitor, to ionic transport across the reactant/electrolyte interface. Because the ionic conductivity inside an electrochemical cell is much smaller than the electronic conductivity in the external metallic circuit, a rechargeable battery cell is fabricated with large-area electrodes separated by a thin electrolyte; a liquid electrolyte requires a separator permeable to the working ion that prevents electronic contact between the electrodes inside the cells. The electrodes can have some thickness provided all the active volume of each electrode makes electronic contact to a metallic current collector that concentrates the electrons of the chemical reaction to/from a contact to the external circuit at each electrode. At open external circuit, ions can still flow inside a cell to equalize  $\mu_A$  and  $\mu_C$  of the electrodes by creating an electric field across the electrolyte; this process charges the cathode positive at the  $V_{oc}$ .

In addition, the electrolyte has an energy gap  $E_g = \text{LUMO} - \text{HOMO}$  between the energies of its lowest unoccupied and highest-occupied molecular orbitals. In a solid electrolyte, this energy window is the  $E_g$  between the bottom of the conduction band and the top of the valence band of the electronic insulator. For a stable, fast charge and discharge, the electrochemical potentials  $\mu_A$  and  $\mu_C$  of the two electrodes need to have energies within  $E_g$  of the electrolyte. Without a kinetic barrier to ionic charge transfer across the electrode/electrolyte interface, a  $\mu_A > \text{LUMO}$  reduces the

electrolyte; similarly a  $\mu_C < \text{HOMO}$  oxidizes the electrolyte. The  $E_g \approx 1.23$  eV of water restricts the voltage, including kinetic barriers, of a rechargeable fuel cell or battery with an aqueous electrolyte to  $V \lesssim 1.5$  V.

Organic liquid electrolytes having an  $E_g \approx 3$  eV allow a stable rechargeable cell having a  $V \approx 3.2$  V; but the working ion must then be an alkali  $\text{Li}^+$  or  $\text{Na}^+$  ion since the  $\text{H}^+$  ion is not sufficiently mobile at room temperature in non-aqueous liquid electrolytes. However, metallic Lithium and Sodium anodes have a  $\mu_A$  above the LUMO of known organic liquid electrolytes and plating of Lithium or Sodium anodes on charge with an organic liquid electrolyte results in the formation and growth of anode dendrites; growth of a dendrite across the electrolyte to the cathode introduces an internal short-circuit with incendiary consequences in a flammable organic electrolyte. Nevertheless, primary Lithium batteries are used where an additive to the liquid electrolyte forms, on reduction of the electrolyte, a passivating  $\text{Li}^+$ -permeable solid-electrolyte interphase (SEI) layer on the surface of a Lithium anode. However, in a rechargeable Li-ion cell with a liquid electrolyte in contact with the anode, charging creates a new Lithium surface area with dendrite formation and growth. Moreover, the SEI layer creates an additional hurdle for  $\text{Li}^+$  transport between the anode and the electrolyte. To circumvent this problem, Li-ion batteries are fabricated in a discharged state with an anode containing no Lithium. Initially, the anode was graphitic carbon with a  $\mu_A$  about 0.2 eV below the Fermi energy ( $\mu_A$ ) of Lithium; but on a fast charge, a  $V_{ch} > \mu_A$  of Lithium plates Lithium on the surface of the carbon. The combination of an SEI layer, a restriction to  $\text{LiC}_6$  of Lithium insertion into graphite, and a slow recharge rate makes this anode solution impractical for the battery of an electric vehicle or for electrical-energy storage for the grid. The introduction of other Li-ion insertion-compound anodes that provide a fast, safe charge have a  $\mu_A > 1.2$  eV below the Fermi energy of Lithium, and the resulting loss of cell voltage reduces the energy density of a cell for a given cathode. To reduce this voltage loss, alloys of Lithium with silica, tin, or antimony have been investigated as anodes, but a large volume change in a charge/discharge cycle makes it necessary to use small alloy particles imbedded in a large volume of, or within a shell of, electronically conducting carbon. Moreover, a  $\mu_A > \text{LUMO}$  still requires formation of an SEI layer, particularly on the initial charge, and the SEI layer traps irreversibly  $\text{Li}^+$  or  $\text{Na}^+$  ions from the cathode, reducing the cathode capacity. A reversible Li or Na alloy may yet be cleverly designed to accommodate the large alloy volume changes; but to be competitive, the solution must only allow SEI formation on the initial charge with sacrificial working ions supplied by a cathode additive. It appears that a solid  $\text{Li}^+$  or  $\text{Na}^+$  electrolyte that is not reduced on contact with a metallic Lithium or Sodium anode can allow reversible plating of a Lithium or Sodium anode across the solid–solid interface, but the plating polarization and overpotential, capacity, and cycle life have yet to be fully investigated and optimized. If the anode problem can be solved, there are many plausible options for the cathode that can make low cost, rechargeable batteries a viable alternative to energy storage in a fossil fuel.

## 5. Prospects for rechargeable batteries

There are two large potential markets for rechargeable batteries: (i) batteries to power electric vehicles (EVs) that can compete with automobiles powered by the internal combustion engine with its distributed, polluting gas emissions and (ii) stationary central and/or distributed batteries that store for the grid electrical energy generated from solar and/or wind energy. Both of these applications must compete with the energy stored in a fossil fuel.

Safety is the first requirement, particularly for portable batteries in EVs and airplanes; cost is the second major hurdle. Cost considerations should include material supply and recycling, manufacture, battery maintenance and life, and environmental compatibility. For portable batteries, additional considerations are volumetric density of the stored energy and the temperature range of acceptable performance. For stationary energy storage the temperature range of operation can be controlled and external chemical energy storage is an option.

### 5.1. Safety

It is argued by some that use of an organic electrolyte is intrinsically unsafe, which would limit rechargeable batteries containing a large stack of cells to those that are all-solid-state or to those with a non-flammable aqueous or ionic-liquid electrolyte. It will be difficult to obtain a competitive, low-cost cathode capacity having an acceptable rate of charge/discharge with an all-solid-state battery since the volume changes of an insertion-compound cathode over a charge/discharge cycle are not conducive to retention of a low energy barrier to ionic transport across a solid–solid interface where the two solids keep changing their relative volumes. On the other hand, an all-solid-state electrochemical capacitor is viable since the volume changes of the electrodes and electrolyte of a capacitor are minimal on cycling. Moreover, realization of a reversible plating through a solid electrolyte of an alkali-metal anode onto a current collector should be possible where the volume change of the electrode is only perpendicular to the electrode–electrolyte interface. A solid electrolyte that plates reversibly a solid anode would eliminate safety problems with anode dendrites and would also act as a supported separator of the anode from a liquid catholyte to open up several cathode options provided the solid electrolyte is stable in the liquid catholyte. The amount of liquid catholyte needed can be too little to pose a major safety hazard. The key to safety of a rechargeable battery stack of large energy density appears to be the ability to plate rapidly and reversibly a metallic anode onto the anode current collector through a solid electrolyte that is stable in a liquid catholyte on the opposite side.

### 5.2. Cost

Abundant materials that are environmentally friendly are preferable for the battery components. Sodium is cheaper and more accessible than Lithium, but cathode options are greater for Li-ion batteries than for Na-ion batteries and  $\mu_A$  of Lithium is 0.3 eV higher than that of Sodium. The principal costs of the large-scale rechargeable batteries are fabrication, cycle life, cell management, and storage efficiency. Simplicity and temperature of cell fabrication are critical considerations. The larger the density of stored energy in a cell, the fewer the number of cells that are needed in the battery stack; elimination of the anode SEI layer can extend cycle life; and elimination of gas emissions and rate constraints on overcharging can simplify cell management of a stack of cells in a large battery. It is possible that cost-competitive Li-ion batteries for EVs will be available within the next 5 years.

### 5.3. Energy density

A rechargeable battery that powers on EV needs a high volumetric energy density  $< V(q) \cdot Q(I)$ . A  $\langle V(q) \rangle \lesssim 5$  V is dictated by the “window” of the electrolyte and/or the difference  $\mu_A - \mu_C$  in the electrochemical potentials of the two electrodes. For a given cathode, the maximum volumetric energy density of a battery cell would be obtained with an alkali-metal anode. Reversible plating of an alkali-metal anode through a solid electrolyte is possible, as

has been demonstrated in all-solid-state rechargeable batteries, but cycle life and rates of charge/discharge with a solid-anode/solid electrolyte interface have yet to be determined for a solid alkali-ion electrolyte of high conductivity over the ambient temperature range that may be experienced by an EV. A low-cost, water-solvated glass/amorphous  $\text{Li}^+$  and/or  $\text{Na}^+$  solid electrolyte that can be conveniently applied to a large-surface-area copper current collector has been reported, but reversible plating of a high-capacity alkali-metal anode with these electrolytes has not yet been demonstrated.

Alternatively, use of a metallic Li or Na alloy can be used; insertion/extraction of the alkali atom into a metal to form an alloy is without dendrite formation, but huge volume changes of the anode particles pose a problem. Moreover, realization of a fast charge without plating of the alkali metal requires a sacrifice of at least 0.5 V in the cell  $\langle V(q) \rangle$  for a given cathode; and unless the voltage is reduced by 1.2 V with present organic liquid carbonate electrolytes, formation on the initial charge of a passivating SEI layer on the anode surface requires sacrificing an irreversible incorporation of the working ion from the cathode in the SEI layer. Moreover, on subsequent cycles in which the alloy is contacted by the liquid electrolyte, new alloy surface area is created that needs new SEI passivation with each cycle, which contributes to capacity fade on cycling. One solution to this problem has been encapsulation of the anode alloy particles in a thin-shelled carbon sphere with enough internal space in the sphere for volume changes of the anode alloy without cracking of the encapsulating carbon sphere, which is permeable to the working ion. The SEI layer forms on the surface of the carbon spheres, which do not change their area in a charge/discharge cycle. With this strategy, the sacrificial working-ion irreversible loss from the cathode capacity on the initial charge can be mitigated by supplying the sacrificial working ions with a cathode additive.

The cathode of a rechargeable battery that powers an EV will probably retain the product of the chemical reaction of a cell; an external store of the product offers a larger capacity for a stationary battery where the volumetric capacity is not critical. With the reaction product contained in the cathode, the voltage of a Li-ion cell with a metallic lithium anode may approach 5 V, but the volumetric capacity of a high-voltage cathode will be limited. On the other hand, with a solid electrolyte interfacing an alkali-metal anode, the soluble  $\text{Li}_2\text{S}_x$  intermediates of the reaction  $16\text{Li} + \text{S}_8 = 8\text{Li}_2\text{S}$  of a Lithium–Sulfur cell would be blocked from reaching the anode, and the modest voltage of the reaction can be more than compensated by a large capacity. It thus appears that an all-electric EV can be expected to provide a driving range of at least 300 miles between charges.

## 6. Perspective for electrochemical capacitors

Low-cost electrochemical capacitors provide a fast charge/discharge, but their capacity is less than that of a rechargeable

battery. The volumetric capacity depends on the electrode–electrolyte interface area per unit volume; it may be increased by increasing the charge on the mobile ion of the liquid electrolyte. Yet to be studied are safe, low-cost all-solid-state capacitors with a water-solvated glass/amorphous solid  $\text{Li}^+$  or  $\text{Na}^+$  conductor also containing mobile  $\text{OH}^-$  anions; these materials have an exceptionally high permittivity. Nevertheless, electrochemical capacitors can be expected to continue to be used as a complement to storage of electrical energy in a rechargeable battery.

## 7. Perspective for fuel cells

The voltage of a fuel cell is limited to  $V < 1.5$  V because it uses an aqueous technology. The low conductivity of the oxide ion ( $\text{O}^{2-}$ ) in a solid oxide fuel cell (SOFC) limits the temperature of operation to  $T_{op} \gtrsim 500^\circ\text{C}$ , which is not competitive for electrical energy storage. Unless liquid methanol can replace gaseous hydrogen as the fuel of a room temperature hydrogen fuel cell, a fuel cell cannot be expected to compete with the rechargeable battery for powering an EV even if the unstable and costly separator and noble-metal catalysts of the PEM (proton-exchange membrane) room-temperature fuel cell are replaced by less costly components. On the other hand, if a low-temperature protonic fuel cell can be inverted to electrolyze steam to supply industry with  $\text{H}_2$  gas at a cost competitive with the high-temperature water–gas shift reaction with a fossil fuel, the charging electrolysis mode of a protonic fuel cell could be an important component of a new energy-technology mix that frees modern society from its dependence on fossil fuels.

## 8. Summary

The challenge of liberating society from its dependence on fossil fuels requires not only energy conservation, but also novel electrochemical technologies. Although meeting the challenge is proving difficult, it appears that it can, as it must, be doable. The development of safe, low-cost rechargeable batteries and electrochemical capacitors of high energy density can displace the internal combustion engine from the increasing fleet of automobiles that produce distributed air-polluting gas emissions, thereby also reducing land and ocean pollution from oil extraction and distribution. Stationary rechargeable batteries for storing for the grid electrical energy generated by solar and wind energy would relieve air and land pollution from coal and gas combustion and extraction as well as disposal of radioactive wastes from nuclear plants. Supplying distributed electric power to isolated villages would enhance rural life. The production of hydrogen gas for industry by a low-cost electrolysis of water would also relieve the use of a fossil fuel.