Hybrid devices for simultaneous energy conversion and storage

Sergey Shleev

Department of Biomedical Science
Faculty of Health and Society
Malmö University
Malmö
Sweden

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Electric Energy

Fuel

Chemical  Nuclear  Mechanical  Solar  Thermal

Nuclear-  Piezo-  Photo-  Thermo-

voltaic

cells
Fuel Cell Advantages

- high theoretical efficiency
- possibility for miniaturization
- production of pure water from the cathodic process
- high energy density
- and many more
Electrical power generation devices
(continuous power supply to the global energy pool)

Fuel cell

Photovoltaic cell

Nuclear voltaic cell

Thermovoltaic cells
Electrical power generation devices
(continuous power supply to the global energy pool)

Electromechanical systems
such as generators

99% of global electric energy!
efficiency on average 35%
$2000000000000000000000000000000$ J
Direct energy conversion

Abundant elements!
Direct energy conversion
Abundant elements
Renewable catalysts!

Living cells  Organelles  Enzymes
Biofuel cells

Bio-solar cells
Electrical power storage

**Batteries**
Primary
Secondary

**Capacitors**
Conventional
Supercapacitors
Closed Cells versus Fuel Cell

Nowadays often called batteries...

“closed system”

[Diagram of closed system with anode, cathode, and electrolyte solution]

“open system”

[Diagram of open system with anode, cathode, hydrogen, and oxygen]

Total reaction:

\[ 2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O} \]
Zn/Air battery?

Fuel Cell Reactions

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

Anode: \( Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \)

Overall Reaction: \( Zn + \frac{1}{2} O_2 \rightarrow ZnO \)

Mass production!

www.duracell.com
Battery, in electricity and electrochemistry, in strict usage, designates an assembly of two or more galvanic cells capable to convert chemical energy directly into electrical energy.
Galvanic cells

Batteries
Galvanic Cells

Primary – one-time usage

Secondary – many times usage (accumulators)

Several cells in series (to increase voltage) – battery
**Capacitor**, device for storing electrical energy, consisting of two conductors in close proximity and insulated from each other.
**Capacitor**, device for storing electrical energy, consisting of two conductors in close proximity and insulated from each other.

**Conventional capacitor**

**Electronic and ionic isolation**

**Electronic isolation**
Materials Science

Where Do Batteries End and Supercapacitors Begin?

Patrice Simon, Yury Gogotsi, Bruce Dunn

Batteries keep our devices working throughout the day—that is, they have a high energy density—but they can take hours to recharge when they run down. For rapid power delivery and recharging (i.e., high power density), electrochemical capacitors known as supercapacitors (1) are used. One such application is regenerative braking, used to recover power in cars and electric mass transit vehicles that would otherwise lose braking energy as heat. However, supercapacitors have low energy density.

Batteries and supercapacitors both rely on electrochemical processes, although separate electrochemical mechanisms determine their relative energy and power density. During the past 5 to 7 years, the energy storage field has witnessed a dramatic expansion in research directed at materials that might combine the high energy density of batteries with the long cycle life and short charging times of supercapacitors (2). However, the blurring of these two electrochemical approaches can cause confusion and may lead to unwarranted claims unless careful attention is paid to fundamental performance characteristics.

The electrochemical processes occurring in batteries and supercapacitors give rise to their different charge-storage properties. In lithium ion (Li+) batteries, the insertion of Li+ that enables redox reactions in bulk electrode materials is diffusion-controlled and can be slow. Supercapacitor devices, also known as electrical double-layer capacitors (EDLCs), store charge by adsorption of electrolyte ions onto the surface of electrode materials (see the figure, panels A to D). No redox reactions are required, so the response to changes in potential without diffusion limitations is rapid and leads to high power. However, the charge is confined to the surface, so the energy density of EDLCs is less than that of batteries (3).

As shown in the figure, panels E to H, supercapacitors can be distinguished from batteries by both potentiostatic and galvanostatic methods. The different methods for achieving double-layer capacitance are characterized by classic rectangular cyclic voltammograms (panel E) and a linear time-dependent change in potential at a constant current (panel G). In batteries, the cyclic voltammograms are characterized by faradaic redox peaks, often with rather large voltage separation (greater than 0.1 to 0.2 V) between oxidation and reduction because of phase transitions (panel F) (4). The presence of two phases is indicated by the voltage plateau in galvanostatic experiments (panel H).

In the 1970s, Conway and others recognized that reversible redox reactions occurring at or near the surface of an appropriate electrode material lead to EDLC-like electrochemical features but the redox processes lead to much greater charge storage.
Capacitors

Conventional

Supercapacitors (electrochemical)

Electrochemical capacitors

- Double-layer capacitors
  - $C_{dl} > 0$
  - $C_\phi = 0$

- Pseudocapacitors
  - $C_{dl} \geq 0$
  - $C_\phi > 0$

Hybrid capacitors
Fuel Cells vs. Capacitors versus Batteries

- Fuel cells
- Conventional batteries
- Ultracapacitors
- Conventional Capacitors

Energy density (Wh/kg)

Power density (W/kg)
General importance of hybridisation

- Energy harvester
- (Power conditioning)
- Energy storage

Hybrid device
- Power management
- Electrical application

Simplifies the design and enables more efficient and miniature power supply

Matches the power need of many electrical applications
Nano Composite

nanoparticles

nanotubes

graphene

PANI-CNTs

PEDOT-graphene/CNTs/GOx
Double function electrodes
simultaneous generation and storage of electric power
Charge/discharge curves of a membrane-based HEPD consisting of a PANI/CNTs based anode and a PtNPs/PPy/CNTs based cathode in separate solutions with pH 7.4. 1 – device equilibration in air saturated buffer, without ascorbate, 2 – addition of 1 mM ascorbic acid to the anolyte, 3 – discharging at a constant load of 10 kΩ, 4 – disconnecting the load, 5 – O$_2$ bubbling through cathodic compartment; 6 - discharging at a constant load of 10 kΩ, 7 – disconnecting the load, 8 – increasing the concentration of ascorbic acid to 2 mM, 9 – discharging at a constant load of 2 kΩ, 10 – disconnecting the load; 11- discharging at a constant load of 2 kΩ; 12 - disconnecting the load; 13 - discharging at a constant load of 2 kΩ.

Characteristics of membrane FC operating separate solutions with pH 7.4. Catholyte was O$_2$ saturated, anolyte contained 1 mM ascorbic acid.
The very first intrinsic hybrid device

Recieved
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A hybrid electric power device for simultaneous generation and storage of electric energy†

Dmitry Pankratov,¹‡ Peter Falkman,³ Zoltan Blum³ and Sergey Shleev²*¹

We herein report on an entirely new kind of electric power device. In the hybrid device, chemical energy is directly converted into electric energy, which is capacitively stored within a singular contrivance. The device is built based on dual-function electrodes, viz. discrete electrodes manifesting simultaneous electrocatalytic and charge-storage features.

Introduction

Ever since M. Faraday and J. Henry discovered electromagnetic induction, there have been continuous developments in electric power generation. Still, almost 200 years later, more than 99% of the electric power produced worldwide is based on the electromagnetic induction phenomenon,¹ and even though electricity is secured from various different sources, including chemical, nuclear, wind, and hydroelectric energies, the critical step is associated with mechanical generators. However, owing to overall mechanical losses, even in 2013 the conversion efficiency can be as low as 5%. This astonishingly low number can also be attributed to the fact that almost 90% of the global electric energy is generated by combustion processes or using nuclear power;¹ i.e. indirect transformation of chemical or nuclear energies into electric energy via thermal and mechanical energies. However, owing to the characteristics of thermal energy, losses during the transformation of thermal energy into work cannot be fully eliminated by any kind of technical development (Carnot theorem).

Indeed, according to the International Energy Agency, in 2012 about 65% of the primary energy used for electricity generation was dissipated as heat.² Despite the fact that the awareness of global warming is rapidly rising and alternative energy sources are desperately sought for, viable alternatives to combustion and/or electromagnetic generation are few and far between.³ Attempts to replenish the pool of global electric energy using exploatory and also more developed devices, e.g. nuclear voltaic cells,⁴ photovoltaic and thermovoltaic cells, as well as combinations thereof,⁵ have been met with quite limited success; apart from various practical and fundamental issues, the energy conversion efficiency of these cells is also low and hence, their present contribution to the global electricity generation is negligible.

Fuel cells (FCs) are electric power generating devices, which directly transform chemical energy into electric energy, and thus, the efficiency, at least theoretically for certain reactions with ΔS < 0, can be even higher than 100%, if the ambient medium heat is captured.⁶ The conversion efficiency of FCs used nowadays is already in the 40–80% interval,⁷ but next-generation devices are
Nano - Bio - Composite

- Nanoparticles
- Proteins
- PANI-CNTs
- Nanotubes
- Organelle
- PEDOT-graphene/CNTs/GOx
- Graphene
- Cell
The very first self-charging biosupercapacitor

1 mW cm$^{-2}$ vs. 0.01 mW cm$^{-2}$
Biocapacitor vs. Biofuel cell

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Electrochemical biocapacitors

Double-layer biocapacitors

\[ C_{dl} > 0 \]

\[ C_\varphi \rightarrow 0 \]

Pseudobiocapacitors

\[ C_{dl} \geq 0 \]

\[ C_\varphi > 0 \]

Hybrid biocapacitors

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Fuel Cells vs. Capacitors versus Batteries

- Fuel cells
- Conventional batteries
- Conventional Capacitors
- Biofuel cells
- Ultracapacitors

Energy density (Wh/kg)

Power density (W/kg)

1 hour

1 second

0.03 second
Piezoelectric-Driven Self-Charging Supercapacitor Power Cell

Ananthakumar Ramadoss, a,b Balasubramanian Saravananakumar, b Seung Woo Lee, b Young-Soo Kim, c Sang Joo Kim, a,b,c and Zhong Lin Wang*a

School of Mechanical Engineering, Korea University, Seoul 136-713, Korea

School of Mechanical Engineering, Korea University, Seoul 136-713, Korea

School of Material Science and Engineering, Korea University, Seoul 136-713, Korea

School of Material Science and Engineering, Korea University, Seoul 136-713, Korea

School of Mechanical Engineering, Korea University, Seoul 136-713, Korea

ABSABSTRACT: Several devices and systems, including power storage and harvesting systems, are powered by energy conversion and storage devices. These devices can be classified into categories such as solar cells, wind turbines, and piezoelectric devices. Piezoelectric devices are known for their ability to convert mechanical energy into electrical energy. In this study, we fabricated a piezoelectric-driven self-charging supercapacitor power cell using NiO nanowires as the positive electrode and a polyvinylidene fluoride (PVDF)-TiO2 nanocomposite film as the negative electrode. The device was integrated into a smart watch and was able to charge the supercapacitor through mechanical energy generated by the movement of the smart watch. The device was also able to charge a smartphone using the same mechanical energy. These results demonstrate the potential of piezoelectric-driven self-charging supercapacitor power cells for powering electronic devices.
Solar energy

Intermittent power production

Green solar energy
Solar biosupercapacitor

Elena González-Aribas a,1, Olga Aleksejeva a,1, Tim Bobrowski b, Miguel Duarte Toscano c, Lo Gorton d, Wolfgang Schuhmann b, Sergey Shleev a,*

a Biomedical Science; Faculty of Health and Society, Malmö University, Jan Waldenströms gata 25, 21428 Malmö, Sweden
b Analytical Chemistry – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany
c Novozymes A/S, Krogshøjvej 36, 2880 Bagsvaerd, Denmark
d Department of Biochemistry and Structural Biology, Lund University, P.O. Box 124, 22100 Lund, Sweden

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**Abstract**

Here we report on an entirely new kind of bioelectronic device – a solar biosupercapacitor, which is built from a dual-feature photobioanode combined with a double-function enzymatic cathode. The self-charging biodevice, based on transparent nanostructured indium tin oxide electrodes modified with biological catalysts, i.e. thylakoid membranes and bilirubin oxidase, is able to capacitively store electricity produced by direct conversion of radiant energy into electric energy. When self-charged during 10 min, using ambient light only, the biosupercapacitor provided a maximum of 6 mW m⁻² at 0.20 V.

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Supercapacitive Photo-Bioanodes and Biosolar Cells: A Novel Approach for Solar Energy Harnessing

Galina Pankratova, Dmitry Pankratov, Kamrul Hasan, Hans-Erik Åkerlund, Per-Åke Albertsson, Dónal Leech, Sergey Shleev,* and Lo Gorton*


Communication

Photo-Biosupercapacitor


Supercapacitive Photo-Bioanodes and Biosolar Cells: A Novel Approach for Solar Energy Harnessing

In this work, for the first time, the concept of supercapacitive photo-bioanode and biosolar cell (photo-biosupercapacitor) for simultaneous solar energy conversion and storage has been demonstrated. Exploiting the capacitive component significantly improves the electron transfer processes and allows the achievement of a current density of 280 $\mu$A cm$^{-2}$ in the pulse mode.
Implantable power sources

Intermittent power consumption

Implantable cardioverter defibrillator by Medtronic, delivering a high-power pulse when needed
Wearable power sources

Intermittent power generation/consumption

Hybrid devices!
Planned future studies:

“Flexible and renewable biological electric power sources based on nanobiocomposite materials” – focusing on fundamental studies

“Multifunctional biological power sources based on flexible materials for wearable and renewable energy supplies” – implementation in wearables

“High performance cost efficient photoelectric biosupercapacitors reproducibly fabricated with industry-scale throughput” – industry collaboration

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