Capacitors for Energy Storage Technology Applications

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Energy

- Electrical
- Thermal
- Mechanical
- Chemical
- ...

Source → Storage → Use

Battery
Capacitor
Supercapacitor
Why Supercapacitors?

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Battery</th>
<th>Capacitor</th>
<th>Supercapacitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge Time</td>
<td>0.3 – 3 hrs</td>
<td>10⁻⁶ – 10⁻³ sec</td>
<td>1 – 30 sec</td>
</tr>
<tr>
<td>Discharge Time</td>
<td>1 – 5 hrs</td>
<td>10⁻⁶ – 10⁻³ sec</td>
<td>1 – 30 sec</td>
</tr>
<tr>
<td>Energy Density (Wh/Kg)</td>
<td>20 - 100</td>
<td>&lt;0.1</td>
<td>1 - 10</td>
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<tr>
<td>Power Density (W/Kg)</td>
<td>50 - 200</td>
<td>&gt; 10 000</td>
<td>1 000 – 2 000</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>500 - 2000</td>
<td>&gt;500 000</td>
<td>&gt; 100 000</td>
</tr>
<tr>
<td>Charge/Discharge Efficiency</td>
<td>0.7 – 0.85</td>
<td>≈ 1</td>
<td>0.90 – 0.95</td>
</tr>
</tbody>
</table>

Bridging the Divide

Inefficiencies of Regular Battery
• Better at discharging energy than absorbing it
• Shorter lifespan resulting in high replacement cost
• Made of toxic materials - ecologically unfriendly

Benefits of the Enhanced Caps
• Improved speed and cycle efficiency
• Smaller unit size
• Withstand extreme temperatures
• High power density
• More sustainable and eco-friendly
• Complementary secondary source of power
Bridging the Divide

1) Eliminate the use of batteries and engines completely

2) Use ultracapacitors in tandem with batteries
SUPERCAPACITOR APPLICATIONS
Market Overview

Market Size and Anticipated Growth of Ultracapacitors

• 2016
  – Worldwide sales anticipated to reach $901.3 million

• 2020
  – Reach $3.5 billion in revenues

• Ultracapacitors account for 5% of the battery energy storage market
Application Categories

1. Consumer Electronics & Professional Instruments
2. Industrial Machinery
3. Automotive & Transportation
4. Green Technology
5. Uninterruptible Power Supplies (UPS)
Consumer Electronics & Professional Instruments
Consumer electronics sales in 2010 rebounded well and showed little ill-effects from the global economic downturn from the previous year. The industry was led by strong sales growth within tablets, E-readers, OLED TVs and smartphones, amongst others.

Global Consumer Electronics Sales 2008-2015

- Retail volume – billion units
- Retail value RSP (US$ bn – fixed 2010)
Consumer Electronics & Professional Instruments

Current Problems
• Inconsistent power pulses overstretch existing battery technologies
• Demand for increasingly smaller and lightweight systems

Solutions & Benefits
• Quick charge
• Extend battery life or eliminate batteries
• Optimize size and cost
• Improve safety and reliability
• Enhance efficiency
• Green technology with no toxic materials
• High durability and life time
Consumer Electronics &
Professional Instruments

Applications

• Burst-Mode Communications
  – Stock keeping, trading, wireless devices

• Quick Charge Hand Tools
  – Hand-held power tools

• Multi-Function Pocket Appliances
  – Cellphones, PDAs, MP3 players, digital cameras, toys
Consumer Electronics & Professional Instruments

Opportunities
• Many applications of technology
• Always in demand whether for leisure or business
• Steady growth
  – 2011- $280.1 billion
  – 2012- $289.9 billion
  – 1.4% growth

Threats
• Product-specific customization of technology
• Costly to manufacture
• Short amount of time to produce
• Large volumes to supply and tailor
Green Technology

Applications

• Wind
  – Pitch Control Systems
    • Provide burst power to maintain rotor speed or optimize output
    • Lowest lifecycle cost and most reliable power backup
  – Voltage Regulation
    • Recycle cycling and power capability
    • Absorb energy → keep voltage spikes down
    • Release energy → prevent dropouts and smooth voltage on grid
Green Technology

Current Problems

- Growing need for renewable energy sources
- Grid instability
- Variability in wind and solar conditions
- Poor utilization of these resources by 30-50%

Solutions & Benefits

- High durability and reliability
- Backup power in emergency situations
- Short-term bridge power capability
- Wide operating temperature range
Green Technology

Applications

• Solar
  – High tolerance in extreme temperatures
  – Store and dispel energy despite varying conditions
  – Ability to generate energy to manipulate and move panels
Green Technology

PV installations analyzed by major Market - 2010 vs 2011

2010 PV Installations by Major Market
- Rest of U.S.: 26%
- California: 29%
- Next Five States: 30%
- New Jersey: 15%

2011 PV Installations by Major Market
- Rest of U.S.: 20%
- California: 29%
- Next Five States: 34%
- New Jersey: 17%

Green Technology

Opportunities

• Large anticipated growth
  – 2030- Wind will supply 20% of all US electricity
  – 2011 to 2017- $145 billion invested wind turbines in North America

Threats

• High development costs
• Not “widely” adopted
Industrial Machinery
Industrial Machinery

Current Problems

• Severe energy and environmental limitations
  – Ex) Forklift operator- battery depletes, need to battery swap mid-shift
  – Exacerbated in refrigerated warehouse environments
  – Performance of a lead-acid storage battery degrades with decreasing temperature

• Requires heavy fuel consumption
Industrial Machinery

Solutions & Benefits

- Reduce fuel consumption
- Cost efficient
- Additional space
- Lower operational costs
- Regenerative power
- Peak assist $\rightarrow$ high power charge/discharge
- Useable in all weather conditions
Industrial Machinery

Applications

• Port Technology
  – Harbor Cranes
• Heavy construction
  – Forklifts
  – Bulldozers
  – Excavators
• Mining
  – Oil
  – Minerals and Resources
Industrial Machinery

Opportunities
- Always in demand and foundational for other industries
- Global machinery market grossed $409 billion in 2009
- Steady growth
  - 2007-2001- Market growth rate of 1.3%
- Most advantageous sectors are engine and turbine segments
  - Revenues over $149.3 billion and contributes to 36.5% of markets current value

Threats
- Qualification to commercialization ranges from 1-3 years
- Some have even longer design and testing periods
- Slow growth
Automotive & Transportation
Automotive & Transportation

Chart 1.1  Annual Sales of Stop-Start Vehicles, World Markets: 2011-2015

(Source: Pike Research)
Automotive & Transportation

**Current Problems**
- Constantly increasing gas prices
- Demand for greener vehicles
- Trade off of performance and fuel efficiency
- Difficulty operating in cold weather conditions
- Limited life of batteries

**Solutions & Benefits**
- Environmentally friendly
- High power density
- Regenerative power
  - High efficiency braking energy recapture
- Increased reliability in stop-start vehicles
- Performance in extreme temperatures
- Enhances battery life, by absorbing power peaks
Automotive & Transportation

Applications

• Regular/Hybrid/Electric Cars
  – Boost to Start-Stop Technology
    • Provide short bursts of energy to restart motor
  – High Power Consumer Support
    • Support short-term power demands that lower voltage
    • Buffer energy loss with stored energy or supplement peak power demand

• Regenerative Braking Systems
  • Absorb and store energy from braking system → assist in acceleration
  • Takes load off mechanical brakes → reduce maintenance and replacement expense
Automotive & Transportation

Applications

- Bus/Tram/Train/ Truck Starter Systems
  - Eliminate morning idle heat up and jump starting in cold climates
  - Frees up under-hood and step-well space from removing lead acid batteries
  - Enable load stabilization and prevent “brown outs”
Automotive & Transportation

Opportunities

• Largest and lucrative market segment
  – 2016-Growth of start-stop vehicles to reach $355.5 million

• Wide range of application

Threats

• Requires extremely demanding performance, reliability, safety, cycle life, and cost

• Long complex development cycles that span numerous years
Uninterruptible Power Supply
Uninterruptible Power Supply

Current Problems

• Constantly increasing gas prices
• Brown out protection due to slow response time
• Difficulty in predicting battery cell operating life
• Limited life of batteries
• Industrial single-phase controls, power supplies and machinery on the grid, are sensitive to voltage sags and swells and brief interruptions (SS&I) will be more problematic from dirty power

Solutions & Benefits

• Environmentally friendly
• High power density
• Enhanced electrode design can improve brown out performance
• Enhances battery life by absorbing power variances
• Enhances equipment life by cleansing dirty power
Uninterruptible Power Supply

Applications

• Raised floor back up systems
• Cell tower back up systems
• Residential back up systems
• Telecommunications back up systems
• Enable load stabilization and prevent “brown outs” from dirty power on the grid
SUPERCAPACITOR STRUCTURE AND COMPONENTS
Supercapacitor

Pseudocapacitor
Electrochemically (Faradaically)

Double-layer Capacitor
Electrostatically (Helmholtz Layer)

Hybrid Capacitor

Uncharged
Charged

electrolyte
separator
electrode
Electrolyte of Supercapacitor

**Liquid-State Electrolyte**
- Aqueous Organic
  - High ionic conductivity
  - Lack of structural stability
  - Tendency to leak
  - Homogenou system required

**Gel Polymer Electrolyte**
- Liquid electrolyte trapped in polymer network
  - High ionic conductivity
  - Mechanical stability
  - Interfacial stability
  - Poor thermal and electrochemical properties

**Solid-State Electrolyte**
- Inorganic Organic
  - Mechanical properties
  - Interfacial stability
  - Thermal stability
  - Electrochemical inertness
  - Ionic conductivity
Graphene

“Graphene is considered a two-dimensional carbon nanofiller with a one-atom-thick planar sheet of $sp^2$ bonded carbon atoms that are densely packed in a honeycomb crystal lattice.”

Preparation:
1. Solution-based reduction of graphene oxide
2. Chemical vapor deposition (CVD)
3. Micromechanical exfoliation of graphite
4. Epitaxial growth on electrically insulating surfaces

Modified Hummers method

Graphite $\rightarrow$ Graphene Oxide (GO) $\rightarrow$ Graphene

0.5 g powdered flake of graphite
0.5 g NaNO₃
24 mL H₂SO₄

3 g KMnO₄ added slowly
Temp. < 20 °C
35 °C, 1h

40 mL DI water
90 °C

yellow-brown suspension
unexfoliated precipitation

DI water
5 mL H₂O₂

until pH = 7

Preparation methods of polymer/graphene composites

• Nanocomposites:
  1. In situ intercalative polymerization
  2. Solution intercalation
  3. Melt intercalation

• Layer Structure composites
  1. Drop coating
  2. Spin coating
  3. Vapor phase polymerization (VPP) of PEDOT
  4. Chemical vapor deposition (CVD) of graphene
Chemical Vapor Deposition of Graphene

Process Outline

• CVD processing supported by Center for Autonomous Solar Power
• Selection of metal substrate
  • Typical metal substrates are Ni and Cu
• Anneal under partial pressure of hydrogen at elevated temperature
  • Typical anneal and reaction range 900 C to 1100 C
• Expose substrate to gas streams of hydrogen and methane for selected duration
  • Deposit of graphene forms
• Reduce temperature at controlled rate to room temperature.

Film Characterization

• Optical Microscopy
• SEM
• Raman Spectroscopy
  • New Thermo Electron DXR Raman Spectrometer purchased and installed
  • Confocal microscope with 532 nm laser and XY mapping capability
Image 1, 4X4 Raman Mapping of CVD Graphene on Copper Foil with 532nm Laser

Image 2, Optical Image of CVD graphene on Copper Foil

The mapping area is selected in image 2. In image 1, the color in upper right image is related to the intensity of G/2D band, which will show us some information about the graphene layers. The upper left 3D image shows the amazing visual image of the intensity on different locations. The Raman is operated at 532nm laser. Three Raman spectra (Red, Blue, Green) are selected, which represent the three spots on image 2 with the same color.
PEDOT-Graphene Nanocomposite Film

xGnP Graphene Nanoplatelets
xGnP – M – 15 Micromechanical exfoliation of graphite
≈ 5 – 8 nanometers thick, typical surface area of 120 – 150 m²/g

0.1 M EDOT (acetonitrile)
graphene nanoplatelets
sonication
0.1 M FeCl₃·6H₂O (acetonitrile)
stirring, insert the substrate
rinse in DI water
dry at RT
PEDOT-graphene composite film

PEDOT PEDOT – 0.1 wt% Graphene PEDOT – 1 wt% Graphene

SEM images of in situ PEDOT – 0.1 wt% Graphene nanoplatelets (a), in situ PEDOT (b), VPP PEDOT (c) and PEDOT:PSS (d).


Multilayered PEDOT-Graphene Composite Film

Graphene/PEDOT Prototype Cell Design

Factors to study:
• Thickness of composite layers
• Composition of PEDOT/graphene
• Preparation of graphene
• Method of film deposition
Graphene/Barium Titanate Prototype Supercapacitor

Diagram of Double Layer Supercapacitors with BaTiO$_3$ Nanofibers Dielectric Thin Film and Graphene-Coated Al Electrode

Based on the equation of $C = \varepsilon_r \varepsilon_0 \frac{A}{d}$, where $C$= capacitance between two electrodes, $d$= distance between two electrodes, $A$= surface area, $\varepsilon_r$= dielectric constant, we can have a higher energy density and capacitance performance when we introduce BaTiO$_3$ and graphene into our supercapacitors devices.
Why Barium Titanate Nanofibers?

BaTiO₃ is a semiconductor, piezoelectric ceramic
- Low production cost
- Porous nanofibers offer higher surface area-to-volume ratio
- High dielectric constant, which is correlated with grain size

*Arit, G.; Hennings D.; deWith G. J. Appl. Phys. 68, 15 August 1985*
Barium acetate was allowed to stir and dissolve in glacial acetic acid. Following the complete dissolution of the barium acetate, titanium isopropoxide was added. The solution was then combined with a solution of polyvinylpyrrolidone (PVP), and allowed to stir until a uniform, translucent sol-gel was obtained. The sol-gel was then loaded into a glass pipette for electrospinning. After electrospinning, the polymer fibers were allowed to dry overnight on the foil, and then transferred into ceramic boats for furnace calcination in air to decompose the polymer structure, leaving only perovskite barium titanate nanofibers.
Nanofibers can be prepared by application of high voltage between a sol-gel solution electrode, and a collecting surface (aluminum foil). The electrified polymer jet is pulled from the tip of the needle, which contains the sol-gel solution, onto the collecting Al foil.
SEM images of composite polymer nanofibers under different solvent systems (a) 3mL acetic acid; (b) 4mL acetic acid; (c) 3mL acetic acid + 0.2mL DI water; BaTiO$_3$ nanofibers (b) after calcination at different temperatures (d) 500 °C; (e) 580 °C; (f) 750 °C
TEM & XRD

TEM images of BaTiO$_3$ nanofibers after 580°C calcination

TEM images of BaTiO$_3$ nanofibers were collected, which indicated that the fibers were porous with diameter around 150nm. XRD of sample before calcination indicated an amorphous fiber. After calcination at 580°C under air, well-defined BaTiO$_3$ perovskite crystallization peaks with high intensity and no detectable secondary phases appeared.
To prepare the uniform dielectric BaTiO$_3$ film, 2.0mL of butanol was added to 0.50 grams of crystallized barium titanate nanofibers in a ceramic mortar. The contents were vigorously ground, forming a viscous white paste. The paste was then drawn up into a pipette, from where it was dropped onto a spinning aluminum substrate. The aluminum foil substrate was spinning from 400 to 500 revolutions per minute for nine seconds. The substrate was then removed from the spin coater and placed in an oven to dry at 90°C for one hour.
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