Capacitive Storage for Wind Energy Generated by Piezoelectric Polymer Materials

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Introductions

Distributed Energy Storage for Sustainable Energy

Loading shift and peak power generation power generation and capacity

Cycling life and safety tolerance

Micro-grid Energy Storage for Transportation

Energy density and power density 60 mile vs. 30 mile Li battery (200 Wh/kg) for 10,000-20,000 Wh for EV and PHEV Cycling response and operating temperature -30 to 52 °C

Materials Challenges

Cost of materials synthesis for electrodes and electrolytes

Performance response to temperature

...the theoretical specific energy of a lithium thionyl chloride battery is 1420 Wh/L, comparable to the theoretical specific energy of TNT at 1920 Wh/L.

Electrical Energy Storage – EES Devices

Rechargeable Batteries

Electrochemical cell that stores energy in a complex system $E=-G/nF - (RT/nF)ln(a_{product}/a_{reactant})$

Electron and ion transports, activation barrier, impedance of the *electrode interface*

Redox Flow Cells and Fuel Cells

Two parallel electrodes separated by an in exchange membrane, forming two electrolyte compartments storing electrical energy.

The electrolyte solutions charge and discharge at electrodes to generate current.

Electrochemical Capacitors (EC) or Supercapacitors, Ultracapacitors

High specific and volumetric capacitances results from high internal surface area of nanporous carbon electrode and nanosize thickness of double layers

 $E = \frac{1}{2}CV^2$

Batteries: Chemical Energy Storage

Rechargeable batteries

Lead-acid, Nickel, Sodium beta, Lithium

cost, , operating temperature range, volumetric energy density, cycling stability

Materials design needs in the complex system

Cell Voltage and charge storage crystalline and amorphous solids, polymers, aqueous and organic liquids active and passive components

Volume and structural changes of active sites at electrodes heterogeneous electronic structures with boundary conditions

Electrochemical processes charge transfer, charge carrier and mass transport and phase transition at electrode-electrolyte *interface*

Electrode materials approaches

Carbon electrodes replaced by silicon nanowires



Future Nanostructure Silicon Anodes



Silicon nanowire anode

Cui, Nature Nanotechnology, 3, 31 (2008)

Battery Anode Materials

Carbon anodes

 $C_6 \longleftrightarrow LiC_6$

Theoretical capacity: 372 mAh/g

Silicon anodes

 $Si_6 \longleftrightarrow Li_{4.4}Si$

Theoretical capacity: 4200 mAh/g

400% volume expansions

Chan, et al., Nano lett. 7, 490 (2007)

Shorter cycling time, longer life time

Future battery anodes



	Existing Tech.	Future Tech. New Materials	
Mechanism	Intercalation	Displacement/alloy	
Volume change	Small	Large	
Li diffusion rate	Fast	Slow	
Specific capacity	Low	High	

Electrical Power Density – Energy Density Comparison



Ragone chart: EES device energy density vs. power density

Electrochemical Capacitors: Physical Charge Storage

Physical storage for electrical energy with charges on opposite insulator

High charge/discharge rates, Low specific energy unlimited cycle life

High *surface area* of electrode materials

Energy density

$$1/C_{t} = (1/C_{+} + 1/C_{-})$$

High cell voltage output limited by breakdown potential (1-3 V/cell) Chu et al, science, 313, 334(2006)

Capacitor materials

Mixed metal oxides (RuO₂ and IrO₂, MnO₂ and Li₄Ti₂O₁₂) for symmetric capacitors Polymers (PET, PPy and PANi) for symmetric/asymmetric capacitors



Wind and Kinetic Energy Conversions



Wind energy conversion from large balloon or deployable tensegrity polymer structures in folded small towed volumes



Objectives:

Demonstrate prototype multifunctional, lightweight devices and deployable structures, which convert mechanical motion and wind energy to electric power for scientific instruments and personal devices.

•Flexible and multiple degrees of freedom wind and other form of kinetic energy conversions.

•Piezoelectric device constructed with high strain polymers and compliant electrodes, capable of "stretching" in parallel with the target motion.

•Enhancement to emerging high altitude wind energy harvesting devices

Applications of piezoelectric materials in other multifunctional structures

Piezoelectric Polymers for Energy Harvesting



Collage showing (a) an astronaut engaged in typical countermeasure activity, (b) laboratory demonstration of contracted and stretched EAP film with accompanying schematics of operation mechanism of an EAP generator, and (c) a prototype shoe-strike power generator. The similar power generation can be achieved by chest pull exercise equipment.

Piezoelectric Polymer Materials

Poly(vinylidene fluoride) (PVDF) Piezoelectric structures





Pervoskite ceramic structure (PZT -- $^{XII}A^{2+VII}B^{4+}X^{2-}_{3}$)



PVDF has direct piezoelectric and reverse piezoelectric effects

Piezoelectric effect: Reverse piezoelectric effect: {D}: electric displacement vector {T}: stress vector [e]: dielectric permittivity matrix [c^{E}]: matrix of elastic coefficients at constant electric field strength {S}: strain vector [α^{S}]: dielectric matrix at constant mechanical strain {E}: electric field vector

Piezoelectric polymers expand or contract in an electrical field or generate an electrical charge when wind pressure is applied from tunnel

Experimental Set Up for Wind Energy Generation and Storage





Experimental Results of Wind Energy Generation Output



Tapping of PVDF will generate a voltage spike. Peak value depends on the force applied, the sample thickness, and even the boundary conditions of the sample.



Periodic signal is generated due to Karman Vortex Street. Storage capacitor is dismounted; Load resistor equals to 800K ohms.

Precision I-V measurements





Storage capacitor is 4.7μ F; Power is dropping down due to sudden stop of wind flow.

Storage capacitor is $4.7\mu F$; Power is ramping up due to wind flow.

Materials Optimizations

Thickness

$110 \ \mu m$

too stiff; barely move under 15 mph wind without tail attached.

With tail attached, Au-coated sample provides 400 mV

28 µm

flexible; easily vibrate; less number of molecular chains causes less charge

Au-coated sample provides 120~150 mV

$52\ \mu m$

Voltage can go up to almost 700 mV

Orientation

Polarization makes difference between pre-stretched direction 1 and direction 2 $d_{31},\,d_{32}$









Mathematical Analysis of Power Generation and Optimizations

$$P_{\text{peak}} = V^2 / R = (e_{31}AS_1\omega)^2 R / (1 + (\omega CR)^2)$$

- e₃₁: piezoelectric coefficient constant of direction 3 respect to direction 1
- A: sample area
- S₁: sample strain
- R_L: load resistance
- C: sample parasitic capacitor





Nanostructure Electrode Materials for Piezoelectric Conversion



Raman analysis of the structure changes of carbon nanotube electrode in the cleared area, which prevent premature failures of film during actuation



The clearing events prevent premature failures of film during actuation with increasing voltage.

Yuan et al, Advanced Materials, 3, **621-625**, (2008) Yu et al, App. Phys. Lett., **95**, 192904 (2009).



Novel electrodes for improved device performance and efficiency





Conclusions

A prototype of an energy harvestor for wind energy using piezoelectric materials is proposed and demonstrated.

In 20 MPH wind condition, the harvestor, which has area of 4 inch², is able to collect $\sim 1 \mu W$ electrical power.

Optimized thickness and active areas and resistance load are obtained under typical variable wind speed

Other Future Plan

Electrodes

Carbon Nanotube and other alternatives

Fluid dynamics calculation Pressure difference in Vortex Street Coupled simulation of fluid and solid

Circuit improve, measurement Impedance matching calculation Ultra low current measurement



Carbon Nanotube Electrodes: Printable Film Capacitors



(a) Scanning electron microscopy image of as-deposited SWCNT networks. (b) Thin film supercapacitor using sprayed SWCNT films on PET as electrodes and a PVA/H3PO4 based polymer electrolyte as both electrolyte and separator.

Kaempgen, et al, 8, 1872 (2009)



Left: Thickness dependence of the capacitance per area for CNT films comparing a liquid (1 M H_2SO_4) and a gel electrolyte (PVA/ H_3PO_4), *Right:* Dependence of specific capacitance on wt. % of PPy in SWNT-Ppy nanocomposites determined by cyclic voltammetry (open circles) and galvanostatic charge-discharge measurements (closed circles).

Conducting Polymer Composites: Modified Surface States









Capacitors and Hybrid Capacitors



Electrochemical difference between EDLC and Lithium Ion Capacitors

 $1/C_{EC} = (1/C_1 + 1/C_2)$ $1/C_{EC} = (1/C_1 + 1/C_2), C_{EC} \sim C_1 (C_1 << C_2)$

Multifunctional Materials for Capacitive Energy Storage



$$C = \varepsilon \frac{A(1 - 2\nu x)}{h(1 + x)}$$

 ϵ is the effective dielectric permittivity of the composite, A is the electrode area, and v is the Poisson's ratio of the composite

Matrices

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PMMA (only one discussed in this talk)
BECy
PolyDCPD
PMMA- Poly (methyl methacrylate)
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Fillers

Insulating ceramics (BaTiO₃, CaCu₃Ti₄O₁₂ (CCTO), ZrW₂O₈) MWCNT, AI, PANI, Clay, Montmorillonite (MMT)

System	Permittivity	tanδ
40% as-received BaTiO ₃	4.4-4.5	0.003-0.05
Functionalized CNT-COOH	0-93.3	>7.92
CNT-COOH added to BaTiO ₃ composite	8.9-52.8	0.159-265
Composite with GPS-funcionalized BaTiO ₃	11.2-80.8	0.164-26.8
Nanoclay, CNT-COOH, and BaTiO ₃ composite	9.2-9.6	0.004-0.007
Quaternay composite sputter coated with silver	17.0-18.3	0.007-0.10

Energy Storage and Power Transmission

Power supply for low power consumption device, such as wireless sensors and portable devices



> Wireless power transmission for inaccessible devices



Power Storage for Miniature Robotic Devices



Wings could be made by PVDF to provide power and reduce the size of the batteries

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