The objective of this proposal is the hierarchical assembly of piezoelectric and semiconducting ribbons onto a common polymeric platform for thin, flexible energy harvesting. In particular, we aim to reach a target output of 5 mW at 100 Hz. The development of a method for integrating highly efficient energy conversion materials onto stretchable, biocompatible rubbers could yield breakthroughs in implantable or wearable energy harvesting systems. Being electromechanically coupled, piezoelectric crystals represent a particularly interesting subset of smart materials which function as sensors/actuators, bioMEMS devices, and energy converters. Yet, the crystallization of these materials generally requires high temperatures for maximally efficient performance, rendering them incompatible with temperature-sensitive plastics and rubbers. Here, we propose overcoming these limitations by presenting a scalable and parallel process for transferring crystalline piezoelectric ribbons of lead zirconate titanate (PZT) from host substrates onto flexible plastics over macroscopic areas. The ribbons are fabricated from single crystal, stoichiometric films of PZT, allowing for exceptional control over the composition and, consequently, the performance characteristics of these materials.
Biointerface Nanopiezoelectrics

Michael McAlpine
Princeton University
## Milestones (5/5/10–5/5/12)

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Accomplishments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 – PZT Ribbon Fabrication</strong></td>
<td><strong>1 – PZT Ribbon Fabrication</strong></td>
</tr>
<tr>
<td>(a) Optimize film growth</td>
<td>✓ Single-crystal, stoichiometric films have been grown and nanoribbons defined</td>
</tr>
<tr>
<td>(b) Fabrication of ribbons</td>
<td>over 2” diameter areas</td>
</tr>
<tr>
<td><strong>2 – PZT Ribbon Transfer to Plastic</strong></td>
<td><strong>2 – PZT Ribbon Transfer to Plastic</strong></td>
</tr>
<tr>
<td>(a) Optimize transfer to flexible substrates</td>
<td>✓ We have been able to achieve transfer onto a variety of substrates, including elastomers, plastics, and silk, over 2” diameter areas</td>
</tr>
<tr>
<td>(b) Scale transfer process to 2” areas</td>
<td><strong>3 – Charge Constant Metrics</strong></td>
</tr>
<tr>
<td>(a) Maximize $d_{33}$ on MgO by PFM</td>
<td><strong>3 – Charge Constant Metrics</strong></td>
</tr>
<tr>
<td>(b) Maximize $d_{33}$ on plastic by PFM</td>
<td>✓ We have achieved the highest piezoelectric charge constant ($d_{33} = 150$ pm/V) ever on a flexible platform</td>
</tr>
<tr>
<td><strong>4 – PZT Energy Harvesting Device</strong></td>
<td><strong>4 – PZT Energy Harvesting Device</strong></td>
</tr>
<tr>
<td>(a) Interdigitated electrode fabrication</td>
<td>✓ Achieved voltage outputs of 1.5 V (peak-to-peak) and power outputs of 10 mW/cm$^3$ in both stretching and flexing operation modes</td>
</tr>
<tr>
<td>(b) Power output test</td>
<td><strong>5 – Heterogeneous Interfacing With Body</strong></td>
</tr>
<tr>
<td>(a) Integration of piezoelectric nanomaterials directly with the body for energy harvesting</td>
<td><strong>5 – Heterogeneous Interfacing with Body</strong></td>
</tr>
<tr>
<td></td>
<td>✓ Demonstrated interfacing with cells, and direct biointerfacing with cow lungs for implantable on-body energy harvesting</td>
</tr>
</tbody>
</table>
Return on Investment – 1

- Total # of people employed: 1 Faculty (Prof. Michael C. McAlpine), 1 graduate student (Thanh Nguyen, graduating 6/2013), 2 postdocs (Dr. Yi Qi, now at GLOBALFOUNDRIES; Dr. Jihoon Kim, now at AZ Electronic Materials)
- # of new hires as a result of this funding: 1 (Dr. Jihoon Kim)
- # of newly trained scientists in this area: 3 (Nguyen, Kim, Qi)
- # of PhD theses initiated based on this work: 0 (I have only been as assistant professor for 4 years, not long enough to graduate someone yet)
- Discoveries utilized on other efforts / Follow-on funding: The results that we have achieved have led directly to a number of new projects and funding:
  - Army Research Office, “Buckled Piezoelectric Nanoribbons: Morphology, Nanomechanics, and Flexoelectricity,” $120k/yr for 3 yrs ($360k total)
  - Lockheed Martin, “Investigation of Wireless Energy Harvesting,” $50k total
  - Essig-Enright and Insley Blair Pyne Funds, “Studying Neuron Biomechanics via Interfacing with Piezoelectric Nanowires,” $52.5k/yr for 2 yrs ($105k total)
- Patents Filed: 2
Return on Investment – 2

• Papers and Books Published: 6 total:
Invited Presentations Related to This Work:

18. “Biointerfaced Nanodevices,” University of California - Berkeley, 10/2/12 (Berkeley, CA).
14. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” University of Texas at Austin, 3/28/12 (Austin, TX).
12. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” University of Illinois at Urbana-Champaign, 2/16/12 (Urbana-Champaign, IL).
Financials: 1) Percent of funds expended: 100%, 2) Total of funds expended: $347,193, 3) Total of funds remaining: $0
Human Power

Piezoelectricity

Sensor → Compress → Net dipole → Actuator

Mechanical Energy

Electrical Energy
Energy

\[ E \propto d_{33}^2 \sigma^2 V \]

<table>
<thead>
<tr>
<th>( d_{33} ) (pm/V)</th>
<th>PZT</th>
<th>PVDF</th>
<th>Quartz</th>
<th>Bone</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>25</td>
<td>2.5</td>
<td>.25</td>
<td></td>
</tr>
</tbody>
</table>

\[ k_{33} \propto d_{33} \]

PZT > 80% Conversion Efficiency

PZT
Phase Diagram

- **Paraelectric**
- **Ferroelectric tetragonal**
- **Ferroelectric rhombohedral**

Composition:
- 100% Lead zirconate
- 100% Lead titanate

Temperature (°C):
- 500
- 400
- 300
- 200
- 100
- 0

% Composition
Dichotomy
<table>
<thead>
<tr>
<th>VLS Growth – Lack of Catalysts</th>
<th>Confined Templates – Polycrystallinity</th>
<th>Hydrothermal – Stoichiometry</th>
</tr>
</thead>
</table>
Thin Film

Post-anneal at 700 °C
PENCIL

Nickel film

resist microlines (1.6 μm)

Nickel nanowires

(1)

(2)

(3)

35 nm

500 nm
Wafer
PZT NWs

(a) Schematic diagram of the fabrication process:

1. Ni NWs and PZT film are deposited on a substrate.
2. PZT NWs are grown on the Ni NWs.

(b) SEM image of the fabricated PZT NWs, showing a width of 20 μm.

(c) EDS spectrum showing the presence of Si, Pb, Zr, Ti, and Ni.

Energy (keV) vs. Count graph, with peaks at 10.24 keV.
Printing

Body-Powered Devices

Everything we do generates power—about 1 watt per breath, 70 watts per step. This year, Michael McAlpine of Princeton University and colleagues figured out how to turn locomotion into power by embedding piezoelectric crystals into a flexible, biocompatible rubberlike material that, when bent, allows the crystals to produce energy.
Piezoforce Microscopy

\[ d_{\text{eff}} = \frac{A_{\text{VIB}}}{V_{\text{AC}}} \]
$d_{33} = 100 \text{ pm/V}$
Interdigitated
Prototype
Impedance Matching

\[ C_{\text{PZT}} \approx 10 \text{pF} \]

\[ V_{\text{PZT}} \]

\[ C_{\text{op-amp}} : 1.5 \text{pF} \]

\[ V_{\text{out}} \]

\[ C_{\text{meter}} \approx n \text{F} \]

\[ V_{\text{meter}} \]
Power

Power = 10 mW/cm³
## Comparison

| This work               | Voltage: 1.5 V  
|                        | Current: 200 nA  
|                        | Power: 0.3 µW  
|                        | Power Density: 10 mW/cm³ |
| Printed PZT Nanoribbons | Voltage: 1.63 V  
|                        | Current: 20 nA  
|                        | Power: 30 nW  
|                        | Power Density: Unknown |
| Chen, Xu, Yao, Shi     | Voltage: 0.7 V  
| PZT Nanofibers         | Current: 100 nA  
| Nano Letters           | Power: 100 nW  
| 10.1021/nl100812k      | Power Density: 2.8 mW/cm³ |
| Xu, Hansen, Wang       |                                |
| PZT Nanowire Arrays    |                                |
| Nature Communications   |                                |
| 10.1038/ncomms109      |                                |
Failure
Buckling


Parameters

(a) PZT ribbon of thickness `h` is adhered to the PDMS.

\[ X = -\frac{L_0}{2} \quad \text{and} \quad X = +\frac{L_0}{2} \]

(b) Buckled ribbon

\[ x = -\frac{L}{2} \quad \text{and} \quad x = +\frac{L}{2} \]

Pre-strained PDMS

Relaxed PDMS

\[ U^{\text{bend}} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2} E h^3 \left( \frac{d^2 w}{dX^2} \right)^2 dX = \frac{E h^3}{12} \frac{\pi^4 A^2}{L_0^3} \]

\[ U^{\text{mid}} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2} E h \epsilon_{\text{mid}}^2 dX = \frac{1}{2} E h L_0 \left( \frac{\pi^2 A^2}{4 L_0^2} - \frac{\epsilon_{\text{pre}}}{1 + \epsilon_{\text{pre}}} \right)^2 \]

\[ U^{\text{adh}} = W_{\text{ad}} L_0. \]
Waveforms

8% Prestrain

Flat region

2% Prestrain

b

Buckle length (μm)

0.0 0.02 0.04 0.06 0.08 0.10

Prestrain

250 nm

500 nm

C

Amplitude (μm)

0 5 10 15 20 25

Prestrain

250 nm

500 nm
Buckled PZT

- PZT ribbons
- MgO

Pre-stretched PDMS

Buckled PZT ribbons

Released PDMS

Silicone rubber

PZT ribbons

$50 \mu m$

$\text{PZT ribbons}$

$\text{Silicone rubber}$

$\text{PZT}$

$\text{rubber}$
Stretchability
Generator

Fine wires + silver paint

PDMS  Wavy ribbons

Fixed end  Moving end

50 μm

0.25 mA/cm²

Time (Sec)

Current (pA)

Stretch

Release

Time (Sec)

Current (pA)

Stretch

Release
Nanogenerators Tap Waste Energy To Power Ultrasmall Electronics

Tiny devices that convert movements into electricity won’t power cities. But they may soon be efficient enough to power arrays of invisible sensors and hand-held electronics.

—ROBERT F. SERVICE

Power surfing on waves

Wavy strips of piezoelectric materials on stretchable substrates can both withstand larger applied mechanical strain without cracking and harvest energy more efficiently than their flat counterparts.

MIN HYUNG LEE & ALI JAVEY
Local Probing

- PFM cantilever
- Buckled PZT
- Pt bottom electrode

Piezoelectric coefficient (pm/V)

Strain gradient ($10^3 \text{ m}^{-1}$)

Profile of buckled ribbon

Voltage (V) vs. Location ($\mu$m)

Profile of buckled ribbon

Voltage vs. Strain gradient

Voltage vs. Location
Enhancement


Flexoelectricity

\[(P)_i = (d)_{ijk} (\varepsilon)_{jk} + (f)_{ijkl} \nabla_l (\varepsilon)_{jk}\]
Cell Nanomechanics

Piezo-Probing

PZT nanoribbon

ITO electrode

SiN$_x$

Neuron

PPT

20 µm

15 µm

20 µm

15 µm
Viability

- Cells on PZT
- Cells on culture medium

Viability percentages over time:
- 72 hours: 90% (PZT), 80% (culture medium)
- 168 hours: 90% (PZT), 80% (culture medium)

Graph showing membrane voltage and current over time.
Neurointerfacing
Calibration
Quantification

Force ~ 1.5 nN | Deflection ~ 1 nm
Biointerfacing
Thanks

DARPA | ARO | LM | AFOSR | AAF | NSF | IC | DUPONT

Prashant Purohit (Upenn) | Michael Berry (Princeton)