Energy harvesting from ambient energy sources is an increasingly important method of providing power to distributed sensor networks where physical connection to a power source is impractical.[1–5] The best conventional mechanical energy harvesting methods typically rely on piezoelectric materials for the conversion of mechanical energy from ambient vibration sources to electrical energy.[6–8] However, the low energy density of these devices excludes their application in low-frequency and static load sources, with the lowest frequency reported devices limited to between 1 and 10 Hz.[9,10] Here, we show that these frequency limitations can be overcome by exploiting the piezoelectrochemical coupling between mechanical stress and voltage in materials that undergo electrochemically induced volumetric changes. Piezoelectrochemical materials can be expected to produce orders of magnitude more energy per volume than conventional mechanical energy harvesting materials (e.g., piezoelectrics) due to the high energy density associated with Faradaic reactions. We experimentally demonstrate the viability of energy harvesting through the piezoelectrochemical effect by using an off-the-shelf lithium-ion battery cell to convert mechanical to electrical energy under low-frequency loads. Our results enable mechanical energy harvesting at previously inaccessible low-frequency ranges and create an opportunity for further exploration of a new class of materials and structures for optimized mechanical to electrical energy conversion.

To help visualize the limitations of conventional materials in low-frequency mechanical energy harvesting applications (e.g., human locomotion,[11,12] human body functions,[13] or vehicle tires,[14]) we construct a diagram of the relevant parameter space in Figure 1. This figure shows estimates of the combinations of mechanical loading frequency and single cycle energy that would be required to supply power for a given application, assuming a 50 MPa mechanical load source as has been done in previous studies.[15,16] For example, a 50 MPa mechanical load source at 0.01 Hz could be used in sensor applications with a device capable of harvesting $10^{-2}$ J cm$^{-3}$ per cycle. However, the device would require an energy density of 10 J cm$^{-3}$ per cycle to be viable for mobile electronics applications. These applications are determined by comparing average power densities characteristic of each application based on the energy density of a lithium-ion battery divided by application run time. This method eliminates the need to make assumptions about the acceptable size of the power source required for an application. Further details of this analysis are provided in the Supporting Information. Figure 1 shows that the use of electrochemical materials could provide a large increase in single cycle energy density, enabling applications previously inaccessible to conventional materials.

The term “piezoelectrochemical effect” is relatively uncommon and is defined here as a change in equilibrium potential due to an applied mechanical stress. This behavior is exhibited by a material that undergoes a volume change as a result of an electrochemical reaction; such materials are referred to here as piezoelectrochemical materials. Although similar in concept to the piezoelectric effect, it should be emphasized that the piezoelectrochemical effect is a fundamentally different phenomenon owing to its physical origin in the thermodynamics of an electrochemical reaction. This piezoelectrochemical coupling has been studied in a few electrochemical systems, most notably in lithium–silicon alloying systems,[17] lithium–graphite systems,[18] sulfuric acid–graphite systems,[19] and lithium cobalt oxide–graphite battery pouch cells.[20] It should be noted that the piezoelectrochemical effect discussed in this work is distinct from that discussed in previous studies in which the term “piezoelectrochemical” is used to describe a system where a conventional piezoelectric material is used to drive an electrochemical reaction.[21–23]

We describe the coupling here in terms of a coupling factor $k$, which is defined as the change in equilibrium potential $U_0$ of an electrochemical reaction with respect to change in applied stress $\sigma$. As detailed in the Supporting Information, $k$ can also be expressed in terms of the mechanical strain $\varepsilon$ produced from an electrochemical reaction involving volumetric charge $q_v$

$$k = \frac{\partial U_0}{\partial \sigma} = \frac{\partial \varepsilon}{\partial q_v} \quad (1)$$

This expression shows that the coupling between stress and voltage is a consequence of the work of mechanical expansion due to the electrochemical motion of charged species. From Equation (1), large coupling factors are expected from materials that exhibit high rates of volumetric expansion per unit charge. This is analogous to PV work in classic thermodynamic piston–cylinder analyses of ideal gasses, and is similar to other expressions for mechanoelectrochemical coupling derived in the literature.[17,24]

While Equation (1) is derived for the case of uniaxial loading and expansion of a single crystal shown in Figure 2a, the same analysis could be applied for composite structures of piezoelectrochemical materials such as a composite electrode (Figure 2b) or full battery cell (Figure 2c) to arrive at a similar expression. There are many configurations by which a piezoelectrochemical cell...
can be used to harvest mechanical energy; three examples for the case of a uniaxial mechanical load are shown in Figure 2d–f. The single cell configuration (Figure 2d) can be used to spontaneously convert mechanical to electrical energy upon application of a stress as long as the electrode materials are chosen such that the initial cell voltage is 0 V. The dual-cell configuration (Figure 2e) eliminates this electrode material constraint by connecting identical cells such that the net voltage is 0 V. If the 0 V condition is not met, the charge-assist configuration (Figure 2f) can be used for energy conversion by using external circuitry to charge/discharge the cell but is not practical for most applications. Examples of thermal energy harvesting electrochemical cells in the single-cell and charge-assist configurations are described in refs. [25] and [26], respectively. Electrochemical cells have also been previously employed to harvest energy from other sources.[27,28]

An electrochemical cell that exhibits a piezoelectrochemical coupling can be used to convert mechanical energy to electrical energy by discharging the cell at a high voltage induced by an applied mechanical load, and recharging the cell at a lower voltage after the applied mechanical load is removed, as shown schematically in Figure 3a. This process is represented from a thermodynamic point of view in Figure 3b,c, and can be described by the thermodynamic cycle comprising the following four steps:

**Step 1 → 2:** The mechanical stress on a cell with coupling factor $K$ is increased by $\Delta \sigma$, increasing the cell voltage to $K \Delta \sigma$. In this step, reversible mechanical work is done on the cell due to elastic deformation equal to the area under the “Load” curve in Figure 3b.

**Step 2 → 3:** The cell is discharged by $\Delta Q_v$, resulting in a contraction of $\Delta \varepsilon$, where $\Delta \varepsilon$ is the change in engineering strain. During discharge, the cell does electrical work equal to the area under the “Discharge” curve in Figure 3c. Simultaneously, mechanical work is done on the cell as it contracts equal to the area under the “Discharge” curve in Figure 3b.

**Step 3 → 4:** The stress is decreased by $\Delta \sigma$ to the original stress, reducing the cell voltage by $K \Delta \sigma$. In this step, reversible mechanical work is done by the cell equal to the area under the “Unload” curve in Figure 3b.

**Step 4 → 1:** The cell is recharged by $\Delta Q_v$, returning it to its original voltage and strain, and thus completing the cycle. During charge, electrical work is done on the cell equal to the area under the “Charge” curve in Figure 3c. Simultaneously, work is done by the cell as it expands equal to the area under the “Charge” curve in Figure 3b.

The net mechanical work $\Delta W_m$ during this process is the enclosed area in Figure 3b, which is equal to

$$\Delta W_m = \Delta \sigma \Delta \varepsilon \tag{2}$$

$\Delta W_m$ represents a net mechanical work that is done on the system. The net electrical work during this process is the enclosed area in Figure 3c, which is equal to

$$\Delta W_e = K \Delta \sigma \Delta Q_v \tag{3}$$

$\Delta W_e$ represents a net electrical work that is done by the system. Note that in Equation (3),

Figure 1. Schematic of the parameter space relevant to low-frequency mechanical energy harvesting. The dashed lines indicate average powers that can be achieved with the specified combination of cycle energy and loading frequency (assuming 50 MPa). The higher energy associated with piezoelectrochemical materials enables new applications at low frequencies.

Figure 2. Schematic analysis of the piezoelectric coupling in a) a single electrode particle, b) a composite electrode, and c) a full cell. This coupling can be used to harvest mechanical energy by configuring piezoelectrochemical cells in d) single-cell, e) dual-cell, and f) charge-assist configurations.
it is assumed that $K$ is independent of $Q_e$. If this assumption were relaxed, Equation (3) could be replaced with an integral expression without changing the general conclusions of this analysis.

Based on the definition of coupling factor in Equation (1), it can be shown that $\Delta W_m$ and $\Delta W_e$ are equivalent, neglecting any losses. In a practical system, losses will reduce the energy harvesting efficiency such that $\Delta W_e$ is always less than $\Delta W_m$. The sources of loss can be both electrochemical and mechanical, such as overpotentials required to drive the electrochemical reaction and viscoelastic losses during mechanical loading. These losses are rate dependent, such that lower efficiencies are expected for higher rate operation. The above analysis also neglects variation in mechanical properties and piezoelectrochemical coupling with $Q_e$, which could affect the analysis.

To identify and compare promising piezoelectrochemical materials for low-frequency mechanical energy harvesting, we define two figures of merit: single cycle energy density $Y$ and peak power density $p_v$. The single cycle energy density is the energy which can be harvested per cubic centimeter of harvester volume during a single mechanical load/unload cycle. The single cycle energy density can be calculated as

$$Y = \int_{q_1}^{q_0} \sigma dq.$$

In calculating $Y$, the integration limits are chosen such that the material could be cycled spontaneously without requiring external charging hardware. In practice, this means that the change in voltage associated with moving from $q_1$ to $q_0$ must be less than $kT$. Equation (4) shows that high $Y$ materials are associated with high $k$ values and high volumetric capacities. Physically, this corresponds to materials that exhibit high expansion and flat discharge voltage curves, as discussed further in Supporting Information.

As shown schematically in Figure 1 and tabulated in Table 1, piezoelectrochemical materials are expected to have very high values of $Y$, which makes them promising candidates for low-frequency mechanical energy harvesting. Table 1 shows some estimated values for $Y$ for different materials assuming a mechanical loading of 50 MPa. The choice of 50 MPa is somewhat arbitrary, but corresponds to a high stress that is still well below the yield strength of most hard materials and has been used in previous comparisons of mechanical energy harvesting technology.\(^{[15,16]}\) As seen in Table 1, $Y$ values for piezoelectrochemical systems can be expected to be on the order of 100–100 000 mJ cm\(^{-3}\). This is much higher than the theoretical energy limits for the best conventional mechanical energy harvesters, which are made with piezoelectric materials exhibiting 30–40 mJ cm\(^{-3}\), assuming the same mechanical loading.\(^{[15,16]}\) A more detailed description of these calculations is provided in the Supporting Information. Note that higher energy densities than those shown in Table 1 may be possible for piezoelectrochemical systems, as Table 1 only considers the limited piezoelectrochemical-material systems for which relevant experimental data are available.

Another important consideration is the power density of the material, which places an upper bound on the frequencies at which piezoelectrochemical materials could be used to harvest energy from cyclic mechanical loads. The volumetric power density can be expressed as

$$p_v = \frac{nF_{\text{id}}K^3 \sigma^2}{4 R_{\text{gas}} T}$$

where $\alpha$ is specific area (m\(^2\) m\(^{-3}\)), $i_{\text{id}}$ is exchange current density, $R_{\text{gas}}$ is the ideal gas constant, and $T$ is temperature. Details of the derivation are included in the Supporting Information. One can see from this figure of merit that materials with high surface areas, high exchange currents, and high coupling factors are favorable for producing high power.

We can use Equation (5) to estimate the volumetric power density of the materials in Table 1. Lithium insertion materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$ [mV MPa(^{-1})]</th>
<th>$Y$ [mJ cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>x$Ce$</em>{0.9}$</td>
<td>0.033</td>
<td>1850</td>
</tr>
<tr>
<td>Li$<em>x$Ce$</em>{0.1}$</td>
<td>0.062</td>
<td>779</td>
</tr>
<tr>
<td>Li$_x$CoO$_2$</td>
<td>$-0.0095$</td>
<td>834</td>
</tr>
<tr>
<td>Li$_x$Si</td>
<td>0.056</td>
<td>271</td>
</tr>
<tr>
<td>C(HSO$_4$)$_2$</td>
<td>13.5</td>
<td>193 000</td>
</tr>
</tbody>
</table>

Table 1. Table listing the results of single-cycle energy calculations from different materials. Note that all of the anisotropic materials are assumed to be oriented with the highest expansion direction parallel to the loading axis. All calculations assume an applied load of 50 MPa.
such as graphite and lithium cobalt oxide have $i_0$ values on the order of 1 A m$^{-2}$.[29] If we assume a surface area corresponding to 1 µm diameter particles, the expected $p_v$ for these materials is on the order of 0.1 mW cm$^{-3}$. However, we expect materials with higher $K$ values to exhibit higher power densities because power scales with $K^2$. For the case of graphite in sulfuric acid, an assumed exchange current density of $10^{-4}$ A m$^{-2}$ produces an expected power density on the order of 1 mW cm$^{-3}$. This estimate of exchange current density appears to be conservative based on data reported in ref.[30], as discussed in the Supporting Information.

For comparison, piezoelectric energy harvesters typically exhibit $p_v$ values in the µW cm$^{-3}$ to mW cm$^{-3}$ range.[31] Thus piezoelectrochemical energy harvesters are expected to have a relatively high energy density but low power density compared to piezoelectric energy harvesters, complementing the conventional energy harvesting technology. This is physically analogous to the complementary role played by batteries and capacitors in the energy storage space. Note that more favorable $p_v$ values could be obtained for the piezoelectrochemical systems by pursuing nanostructuring strategies to increase surface area, which could reasonably increase the $p_v$ values by one or two factors of 10. It should also be noted that in a practical system, there would also be limitations associated with ion transport in the electrolyte, which could conceivably limit the power of a system containing high surface area electrodes.

To experimentally demonstrate the concept of mechanical energy harvesting through the piezoelectrochemical coupling, we show that an off-the-shelf lithium-ion battery pouch cell can be used to convert mechanical energy to electrochemical energy. Although neither designed nor optimized for mechanical energy harvesting, a pouch cell is expected to exhibit similar behavior to a piezoelectrochemical energy harvester as discussed previously. The off-the-shelf pouch cell is a particularly attractive system for investigation due to the large body of knowledge regarding commercial battery materials as well as the ease with which the materials can be obtained and experiments replicated. The pouch cells are arranged in the Figure 2e dual-cell configuration using a resistor as the electrical load, such that electrical power is spontaneously dissipated by the resistor upon the application of a mechanical stress to one of the cells. The cells are initially charged to 12.5% capacity to maximize the single-cycle energy output of the cell. As shown in Figure 4a,b, this state of charge corresponds to a high combination of coupling factor and capacitance. Knowledge of these two measured properties of the piezoelectrochemical system is most important for maximizing the integral in Equation (4), as discussed further in the Supporting Information. It should be noted that the measured coupling factors in Figure 4b agree well with the expected values from Table 1 for the Li$_x$C$_6$ and Li$_y$CoO$_2$ system.

The 20 µHz cyclic compressive stress shown in Figure 4c is applied to one of the cells and the voltage output across the load resistor is recorded in Figure 4d, which shows an alternating voltage signal of the same frequency as the applied mechanical load. Here, a positive voltage indicates that the voltage of the compressed cell is higher than that of the uncompressed cell, so that the compressed cell is discharged through the resistor. The opposite is true of a negative voltage. With the exception of an initial transient seen in the first cycle, this voltage oscillates about 0 V, indicating that the process is reversible and that charge is being cyclically passed between the compressed and the uncompressed cell during loading/unloading. This voltage signal can be used to calculate the power dissipated by the load.

Figure 4. Plots of a) coupling factor and b) voltage curve slope of the pouch cell used to experimentally demonstrate the working principle of a piezoelectrochemical energy harvester. c) The mechanical load profile applied to the working cell. The electrical output as a function of time delivered to the electrical load is given in terms of d) voltage, e) current, and f) power.
resistor plotted in Figure 4e, which shows peak power outputs for this device of about 0.08 μW. The power can be integrated over time to determine the energy output of the cell, shown in Figure 4f. On a single cycle basis, the power output of the dual pouch cell energy harvester is 0.68 mJ cycle⁻¹. This represents 54% of the maximum theoretical value, which corresponds to approximately a 1% deviation in state of charge from the optimal as discussed in further detail in the Supporting Information.

While the pouch cell system demonstrated here represents a proof of concept, there is clearly room for optimization. For example, the Li₂CoO₂ and Li₄C₆ electrodes could be lithiated to the optimal concentrations listed in Table 1 prior to cell assembly to optimize the expected energy output. Beyond the graphite/lithium cobalt oxide system, other systems with higher coupling factors such as the graphite + HSO₄ could offer significantly higher energy densities, as predicted by the calculations in Table 1. Nanostructuring the electrodes could also help reduce the power losses associated with overpotentials, thereby increasing the power that can be delivered to a load. These material considerations can be combined with previously discussed harvester design strategies to further enhance device performance by optimizing system geometry and coupling with respect to the applied stress tensor. Thus the work presented here represents a starting point and roadmap for developing piezoelectrochemical energy harvesters, which could enable mechanical energy harvesting at previously inaccessible low frequencies with further design optimization.

**Experimental Section**

The pouch cell couple consists of two commercially available 240 mAh cells containing lithium cobalt oxide (Li₂CoO₂) and graphite (Li₄C₆) electrodes with an electrolyte of lithium hexafluorophosphate in organic solvent. The cell’s electrodes are composite films of micrometer-scale active material particles bound with a polymer binder. The cells are set to the same voltage by connecting the two cells in a parallel configuration. The desired initial state of charge (SOC) is selected based on measurements of coupling factor and cell capacitance. The coupling factor as a function of SOC is determined using the process described in ref. [20] in which the rate of change in voltage with respect to applied stress is measured during the application of a linear compressive stress ramp. The capacitance plotted in Figure 4b is the inverse of the slope of the discharge curve of a single 240 mAh battery cell during a 12 mA discharge. The highest combination of capacitance and coupling factor is found to occur around an SOC of 12.5% in the cells considered in this work.

The initial SOC is set to 12.5% by discharging the parallel-connected cells at 240 mA to 2.7 V and then charging at 240 mA for 900 s. The parallel-connected cells are allowed to rest until the cell voltage no longer varies in time due to relaxation of internal concentration gradients. The cells are then configured into the dual-cell harvester configuration by shorting the negative terminals together and removing the positive terminals with a 10 Ω resistor (which is approximately impedance-matched with the harvester) to simulate an electrical load. The voltage across the 10 Ω resistor is monitored and used to exhibit a stable 0 V output (indicative of no power output) for 4 h. A cyclic 20 μHz compressive stress square wave is applied to a single cell of the couple using a universal compression testing machine containing spherically seated platens to maintain good alignment. A 0–20 MPa stress range is chosen to avoid damaging the cell, as stresses in excess of 20 MPa lead to internal shorting and general mechanical damage in these cells due to separator deformation. [31] During mechanical loading, the voltage across the resistor is monitored and used to determine the electrical output of the harvester.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

Received: June 19, 2015
Revised: August 31, 2015
Published online: