

# Characterization and Model of Piezoelectrochemical Energy Harvesting Using Lithium ion Batteries

Z.J. Schiffer<sup>1,2</sup> · C.B. Arnold<sup>1,3</sup>

Received: 22 August 2016 / Accepted: 24 April 2017  
© Society for Experimental Mechanics 2017

**Abstract** Although lithium ion battery research often focuses on electrochemical properties, lithium ion intercalation materials are also mechanically active. Essentially, these materials exhibit a mechanical-electrochemical coupling such that when a stress is applied, the voltage of the battery increases. In this work, we develop a model to study and predict the effectiveness of intercalation materials as mechanical energy harvesters. Specifically, we show that a lithium ion battery harvester can be modelled as a simple circuit and that we can make both qualitative and quantitative predictions about the effectiveness of a battery material given its intrinsic mechanical and electrochemical properties. The measured efficiency of our system, calculated from the energy output and total work input, is  $0.012 \pm 0.004\%$ , and our model predicts that the maximum theoretical efficiency of the system is  $2.9 \pm 0.5\%$ . In the future, this model will help us develop and study other intercalation materials that will bring the measured efficiency closer to our proposed theoretical maximum.

**Keywords** Piezoelectrochemistry · Lithium-ion batteries · Mechanical energy harvesting · Mechanical-electrochemical coupling

---

✉ C. B. Arnold  
cbarnold@princeton.edu

<sup>1</sup> Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, NJ, USA

<sup>2</sup> Department of Chemical Engineering, MIT, Cambridge, MA, USA

<sup>3</sup> Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA

## Introduction

Batteries are the prototypical accessible storage device, and lithium ion batteries are among the most useful due to their high energy density and low rate of self-discharge [1]. Lithium ion batteries are found in devices ranging from cell phones to electric vehicles and will continue to remain important for these and other energy storage applications in the future. In this work, we investigate batteries from a nontraditional perspective: as a tool for energy harvesting. Specifically, this work focuses on how lithium ion batteries can be used to convert mechanical work into electrical energy, a property that has not been explored in detail. Our primary goal is to characterize the mechanical energy harvesting process in piezoelectrochemical systems, and in the course of this work we also propose a model to help select and optimize piezoelectrochemical systems in the future.

Recent work on battery electrode mechanics has investigated how applied stresses and strains can affect electrochemistry for various systems, including lithium-silicon, lithium-graphite, and sulfuric acid-graphite [2–8]. Previous research uses rigorous thermodynamic models to derive a linear proportionality between a change in stress and the equilibrium potential of lithium ions for silicon anodes [5–7]. The results of this previous research were extended to graphite electrodes, and a simple conservation of energy model finds a similar linear correlation between applied stress on a battery and a corresponding increase in voltage [2]. These results and others that measure stress as a function of voltage indicate that there is a fundamental coupling between battery mechanics and electrochemistry [7].

In this work, we leverage the idea that one can take an off-the-shelf lithium ion battery, squeeze it, and then see an increase in the voltage (of order 0.1 mV). While this has only been tested with commercial lithium ion batteries, this concept

should apply not just to lithium ion batteries, but to any intercalation material [2]. Using this phenomenon, intercalation materials can be useful as stress sensors because they do not require a power source and have a flexible design shape, but they are unlikely to be widely utilized in this capacity because extremely large stresses (order MPa) are necessary to produce very small voltages [2].

Nevertheless, the coupling between mechanical stress and electrochemistry can be utilized in energy harvesting applications. Currently, piezoelectric materials are the most common materials for converting mechanical to electrical energy, often using high-frequency vibrations from the environment to produce electrical energy [9, 10]. Piezoelectric materials, though, do not work very well for low-frequency mechanical oscillations below 1 Hz [11, 12]. Battery intercalation materials, or “piezoelectrochemical” materials, take advantage of the stress-voltage coupling in intercalation materials and harvest energy at extremely low frequencies (less than 1 mHz). Additionally, piezoelectrochemical materials have a higher energy density per unit volume than traditional piezoelectric materials [13]. In previous research, we used two antiparallel lithium ion batteries connected through an external load to demonstrate how to harvest small amounts of energy by squeezing one battery [13]. Other research groups have demonstrated alternative geometries using silicon electrodes that can harvest energy with similar mechanisms [14]. In this paper, we develop a model to study the piezoelectrochemical harvesting process with lithium ion batteries and then use this model to characterize the harvesting system and determine its maximum theoretical efficiency. Our model leverages the fundamental coupling between mechanics and electrochemistry in battery materials and can be applied to other intercalation materials to predict their effectiveness for energy harvesting applications.

## Experimental Methods

Our primary energy harvesting setup consists of 170 mAh pouch cells containing LCO and graphite electrodes. State of charge measurements are based on the 170 mAh nominal capacity, and batteries are charged to a given state of charge after discharging to 3 V and holding at 3 V until the current decays under 1 mA. These cells are manufactured by AA Portable Power Corp and have a nominal size of 25 mm by 20 mm by 5 mm. They are compressed using an Instron mechanical characterization tool to a known stress (calculated as force per unit area) and voltage measurements are taken with a Solartron potentiostat. All strain measurements and derivatives are measured and analyzed as described in previous research [15]. Specifically, an LVDT is used to measure strain of a lithium ion pouch cell while an Arbin potentiostat performs

a constant-current charge at  $C/20$ . The derivatives of the data are calculated using MATLAB.

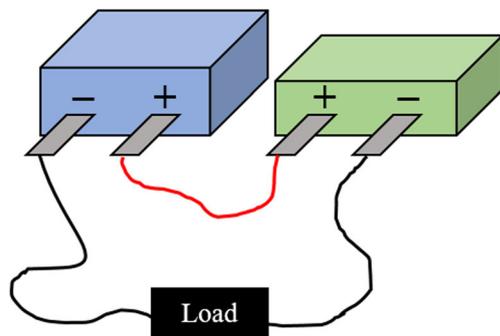
For the characterization harvesting experiments we connect two batteries in anti-parallel with a resistor between two leads and measure the potential drop across the resistor. A schematic of the setup is depicted in Fig. 1 and described in further detail in previous work [13]. One cell is compressed between 0.1 and 10 to 15 MPa in a cyclic pattern depicted in Fig. 2. Note that each cell is cycled at least five times before any measurements are taken to avoid first-cycle inelastic effects. Additionally, measurements are only taken after the initial voltage equilibrates to approximately 0 V ( $< 50 \mu\text{V}$ ). During analysis, the voltage decay is fit with exponential functions using MATLAB and all mathematical analysis is performed in MATLAB and Excel. All error is  $1\sigma$  unless otherwise indicated. Note that the data presented represents a sample of best data acquired and that there can be a large variance in the measured properties due to manufacturing differences between batteries.

## Proof of Concept

Lithium ion batteries exhibit a mechanical-electrochemical coupling such that when a stress is applied, the voltage increases. Specifically, previous research has proposed the following relationship.

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

Where  $\Delta V$  is the voltage change of the battery,  $\varepsilon$  is the total mechanical strain of the battery,  $q_v$  is the volumetric charge of the battery,  $\sigma$  is a stress (applied by an Instron throughout this work), and  $k$  is a coupling factor defined in equation (1). [2, 13] This coupling is due to mechanical stresses shifting the equilibrium potential of lithium ions in the electrodes, thus changing the voltage [5, 6]. Although a thorough thermodynamic treatment of the electrode will result in the above proportionality, Equation (1) can also be derived from conservation of energy during battery compression. [2, 13] Throughout this work, we will assume that the battery will instantly adjust to the new equilibrium when compressed, i.e., the voltage change is instantaneous compared to other processes and there are no other kinetic processes that could result in energy losses (although electrode fracturing is a potential energy loss mechanism, fracturing is unlikely at 10 MPa and beyond the scope of this work) [16]. The details of this relationship in the context of mechanical energy harvesting are further explored below, but equation (1) is sufficient for a simple proof-of-concept. In the setup shown in Fig. 1, the green cell is compressed, increasing its voltage relative to the blue reference cell. However, because the two cells are connected, the

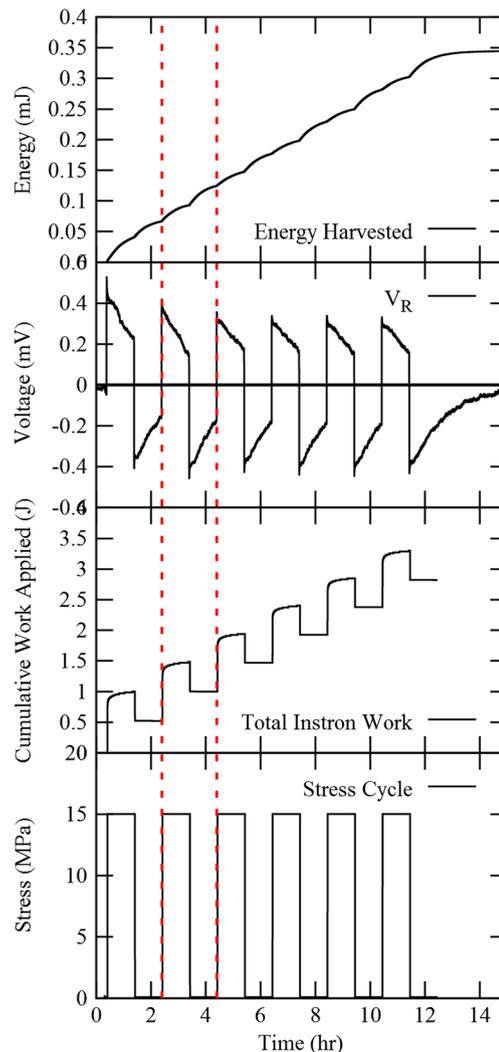


**Fig. 1** Schematic of experimental setup. The green cell is compressed and the blue cell is the reference cell/reservoir [13]

voltage will equilibrate, and power will be consumed by the load. In this particular case, the load is a  $10\ \Omega$  resistor (chosen to maximize power output through impedance matching). [13] Once the voltages have equilibrated, the stress is removed and the voltage of the green cell decreases relative to the blue cell. The cells then equilibrate again, generating power across the load. An example of multiple cycles is shown in Fig. 2, a slight variation on a similar experiment previously described. [13] The cells in this figure are at 20% state of charge because this state of charge is near optimal according to previous research and the cell is compressed to 15 MPa to maximize energy harvesting without destroying the battery. [13] Fig. 2 depicts, from bottom to top, the stress applied as a function of time, the total work done by the Instron over time, the resulting voltage increases, and the energy harvested from each cycle (the integral of the power over the resistor with respect to time). One cycle is marked with vertical dashed lines in Fig. 2.

On average, each cycle during the test shown in Fig. 2 results in  $0.057 \pm 0.002$  mJ of energy (average  $7.9 \pm 0.3$  nW output) and the Instron applies  $0.47 \pm 0.01$  J of work per cycle, resulting in a conversion efficiency of  $\eta_{measured} = 0.012 \pm 0.004\%$ . Note that this is not an idealized system, and similar batteries have efficiencies between 0.01% and 0.2% for this type of energy harvesting [13]. This efficiency represents an unoptimized system, and is comparable to other mechanical harvesters that use mechanical-electrochemical coupling [13]. Future work will hopefully improve this efficiency with optimized materials and procedures.

In Fig. 2, the voltage does not completely decay to 0 V during each cycle because the cycles are limited to a two-hour period in order to perform more tests. Two hours is sufficient to fit an exponential, and by comparing the experimental energy harvested per cycle to the theoretical energy harvested by letting the exponential decay to infinite time, each cycle achieves  $80 \pm 2\%$  of its maximum possible harvested energy if the voltage decayed infinitely. In the end, this experiment demonstrates the feasibility of energy harvesting using this procedure and provides a baseline for future piezoelectrochemical experiments and characterizations.



**Fig. 2** Demonstration of the feasibility of energy harvesting using 170 mAh batteries at 20% state of charge. The plots, in order from bottom to top, are the mechanical stress profile as measured by the Instron, the cumulative Instron work, the voltage across the resistor, and the total energy harvested. The red dashed lines mark a single cycle. Note that the current across the resistor is simply the voltage divided by  $10\ \Omega$  since we are using a fixed resistor

However, to improve and optimize this procedure, we need to understand the underlying mechanical-electrochemical coupling in battery materials better. Specifically, we need to understand the exact mechanisms that are occurring in the simple circuit depicted in Fig. 1.

## Theoretical Model

To model the harvesting, we can treat the schematic from Fig. 1 as a circuit, where the batteries are both at constant state of charge (this is valid due to the extremely small amount of charge transferred between the batteries due to the small voltage difference). In particular, we will treat the batteries as

capacitors which are oppositely polarized, with one battery (the compressed one) at an initial voltage of  $\Delta V$  and both batteries having capacitance described by equation (2). [17]

$$C = \left( \frac{dQ}{dV} \right)_{Q_{SOC}} = \frac{1}{\left( \frac{dV}{dQ} \right)_{Q_{SOC}}} \quad (2)$$

The capacitance described in equation (2) is valid at any constant SOC, and because the flow of electrons around the circuit throughout the harvesting process is negligible compared to the capacity in the battery at any SOC, the capacitance during the process is constant. The circuit is depicted in Fig. 3.

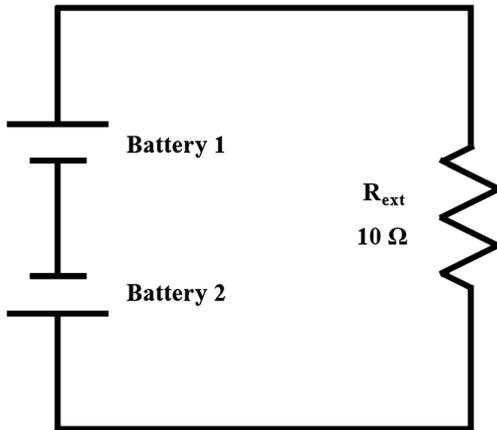
Applying Kirckoff's second law to the circuit in Fig. 3 results in equation (3a). Both batteries in Fig. 3 are at the same SOC and battery 2 is compressed, increasing its voltage by  $\Delta V$ .  $Q$  is the amount of charge lost by battery 2 and gained by battery 1 (i.e.,  $Q$  is the number of coulombs that pass through the circuit). Equation (3a) can be rearranged into equation (3b) and solved for  $Q$  in equation (3c) using the boundary condition that  $Q = 0$  at  $t = 0$ .

$$V_{Bat1} + V_{Bat2} + V_R = -Q \left( \frac{dV}{dQ} \right)_{SOC} + \left( \Delta V - Q \left( \frac{dV}{dQ} \right)_{SOC} \right) - \frac{dQ}{dt} R_{ext} = 0 \quad (3a)$$

$$\frac{dQ}{dt} = \frac{\Delta V}{R_{ext}} - \frac{2Q}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC} \quad (3b)$$

$$Q(t) = \frac{\Delta V}{2 \left( \frac{dV}{dQ} \right)_{SOC}} \left( 1 - e^{-\frac{2t}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}} \right) = Q_{\infty} \left( 1 - e^{-\frac{2t}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}} \right) \quad (3c)$$

The voltage across the resistor is going to be the last term in equation (3a), and voltage as a function of time across the resistor is given in equation (4).



**Fig. 3** A circuit schematic of the setup described in Fig. 1. Note that we will treat the batteries here as “capacitors” because the batteries are at essentially constant state of charge. Also note that the batteries are antiparallel

$$V_R(t) = \frac{dQ}{dt} R_{ext} = \Delta V e^{-\frac{2t}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}} \quad (4)$$

From equation (3c) and equation (4), as  $t \rightarrow \infty$ ,  $Q(t) \rightarrow \frac{\Delta V}{2 \left( \frac{dV}{dQ} \right)_{SOC}} = Q_{\infty}$  and  $V_R(t) \rightarrow 0$ . This means that initially,  $V_R = \Delta V$  but over time, the capacitors charge up to a voltage of  $\Delta V/2$  and the voltage over the resistor decays to zero, as expected when energy is dissipated through the system. Note that the above derivation is for a compressed battery (that is  $\Delta V > 0$ ), but that when the battery is uncompressed, the same process occurs with a negative voltage and negative current, dissipating the same amount of energy over the resistor but with current flow reversed. The total amount of energy dissipated over the resistor is given by equation (5), with a factor of two accounting for both the compression and release steps.

$$\frac{E_{res}}{2} = \int_0^{\infty} \frac{V_R(t)^2}{R_{ext}} dt = \int_0^{\infty} \frac{\Delta V^2}{R_{ext}} e^{-\frac{4t}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}} dt = \frac{\Delta V^2}{4 \left( \frac{dV}{dQ} \right)_{SOC}} \quad (5)$$

Because lithium ion batteries expand and contract, and strain is a strong function of state of charge, we can compare the energy dissipated over the resistor with the energy input of the compressive force as the compressed battery contracts slightly when the charge moves around the circuit [15]. The work input is given by equation (6a), and the conservation of energy equation is given by equation (6b). The applied force is given by  $F_{app}$ , the amount of expansion by  $\ell/\ell_0 = \epsilon$  (using the standard definition of engineering strain), and the capacity of the battery by  $Q$ . We denote the energy losses as  $E_{loss}$ . Equation (6a) represents the theoretical compressive work done by the Instron on the battery, and equation (6b) represents conservation of energy—namely that all compressive work is either lost somewhere in the circuit or is dissipated by the resistor as electrical work. Note that energy is only input during the compression, whereas energy is dissipated through the resistor during both the compression and the release.

$$\begin{aligned} W_{compress} &= \int F_{app} d\ell = \int_{Q_{SOC}}^{Q_{SOC} - Q_{\infty}} F_{app} \left( \frac{d\ell}{dQ} \right)_{SOC} dQ \\ &= F_{app} \left( \frac{d\ell}{dQ} \right)_{SOC} Q_{\infty} \end{aligned} \quad (6a)$$

$$\begin{aligned} W_{compress} &= F_{app} \left( \frac{d\ell}{dQ} \right)_{SOC} \left( \frac{\Delta V}{2 \left( \frac{dV}{dQ} \right)_{SOC}} \right) \\ &= E_{res} + E_{loss} = \frac{\Delta V^2}{2 \left( \frac{dV}{dQ} \right)_{SOC}} + E_{loss} \end{aligned} \quad (6b)$$

$$\Delta V = \alpha F_{app} \left( \frac{d\ell}{dQ} \right)_{SOC} \quad (6c)$$

$$E_{loss} = (1-\alpha)W_{compress} = \alpha(1-\alpha) \frac{F_{app}^2 \left( \frac{d\ell}{dQ} \right)_{SOC}^2}{2 \left( \frac{dV}{dQ} \right)_{SOC}} \quad (6d)$$

$$E_{res} = \alpha W_{compress} = \alpha^2 \frac{F_{app}^2 \left( \frac{d\ell}{dQ} \right)_{SOC}^2}{2 \left( \frac{dV}{dQ} \right)_{SOC}} \quad (6e)$$

$$W_{compress,max} = \lim_{\alpha \rightarrow 1} W_{compress} = \frac{F_{app}^2 \left( \frac{d\ell}{dQ} \right)_{SOC}^2}{2 \left( \frac{dV}{dQ} \right)_{SOC}} \quad (6f)$$

We assume that the efficiency of this system is constant, i.e.,  $E_{loss} = (1-\alpha)W_{compress}$  for some constant  $0 \leq \alpha \leq 1$ . With this assumption, we can solve for the initial voltage (equation (6c)) and the energy loss term (equation (6d)). The limit of  $E_{loss} \rightarrow 0$  is the same as  $\alpha \rightarrow 1$ , which results in  $\Delta V = F_{app} \left( \frac{d\ell}{dQ} \right)_{SOC} = \sigma \left( \frac{d\epsilon}{dq_v} \right)_{SOC}$  [13]. From the conservation of energy, we have rigorously derived an expression for  $\Delta V$  in equation (6c) that matches exactly the expression postulated in equation (1) in the limit of no energy losses. In this derivation, we assume that the measured time constant is exactly  $\frac{2}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}$ . In practice, we find that this time constant is off by a small factor (close to unity)  $\beta$  such that  $b = \beta \frac{2}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}$ , where  $b$  is the measured time constant. Combining equations (6e) and (6f), we determine that the maximum theoretical efficiency for a battery with known parameters alpha and beta is given by,

$$\eta_{theory} = \alpha^2 / \beta \quad (7)$$

## Initial Voltage Peak and State of Charge

In general, there are many parameters that affect the energy harvesting system shown schematically in Fig. 1. In this system, when one battery is compressed, the equilibrium potential changes and lithium ions (and electrons) move to equilibrate the potentials of the two batteries. However, both the equilibrium potential and the mechanics of the system are strong functions of state of charge. State of charge is therefore an extremely important parameter to investigate when considering energy harvesting. Other parameters of interest include: the stress applied (more stress correlates with more voltage) and the load resistance (voltage and power are functions of resistance). To investigate the parameters of the amount of energy harvested, we cycled the system with a period of one hour (enough to fit an exponential) with a stress of 10 MPa

(higher stresses had adverse effects on our particular batteries over time). All averages here represent at least five cycles. The voltage as a function of time was fit to an exponential equation of the form given in equation (8).

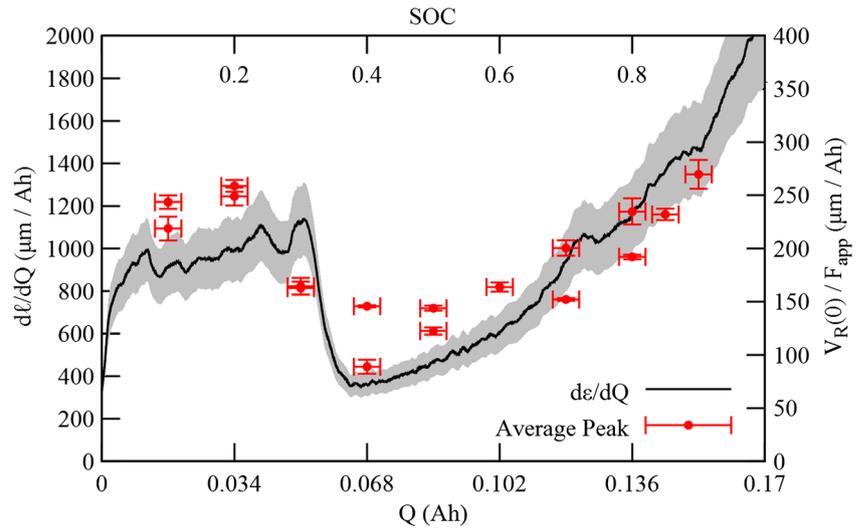
$$V_R(t) = ae^{-bt} \quad (8)$$

Perhaps the most important parameter to investigate as a function of state of charge is the initial change in voltage the system experiences when compressed, represented in equation (8) as  $a = V_R(0)$ . As described in equation (1) and (6c), the factor that determines the voltage increase at a given stress state is equal to the first derivative of strain with respect to state of charge (derived in detail in previous work) [2, 13]. Fundamentally, this derivative has been previously related to electrode phase transitions, specifically the lattice heights and equilibrium potentials of the phases [15]. Other intercalation materials that exhibit phase translations can be easily evaluated for use as an energy harvester with quick mechanical measurements.

The same type of experiment from Fig. 2 (with slight differences described previously) is run at different states of charges, and the average peak heights for multiple cycles ( $V_R(t=0)$ ) are compared to the derivative of expansion in Fig. 4. This comparison is done by comparing  $V_R(0)/F_{app}$  to  $d\ell/dQ$ , quantities that should be proportional according to equation (6c). The y-error for the data points is the result of variations between cycles of the same battery. The x-error for the data points is chosen based on observed variations in maximum capacity of the batteries (and therefore state of charge calculations). The shaded error for the derivative is taken from manufacturer boundaries for the variations in height of the batteries and therefore their expansion and strain. The axes' ranges are picked to best compare the quantities assuming a direct correlation between the data, discussed below. The measured heights and the derivative of expansion agree well have the same general trends. Using a direct fit ( $\alpha d\ell/dQ = V_R(0)/F_{app}$ ), we can solve for the parameter  $\alpha$ , as defined in equation (6c). This fit calculation gives  $\alpha = 0.20 \pm 0.02$ . The energy losses in this process are likely due to friction, heat, and other resistive losses in the system such as increased resistance when the battery is compressed [18]. Along with  $\beta$ , this value can help determine the maximum theoretical efficiency of this system according to equation (7).

In our model, we assume that  $\alpha$  is a constant, but it could be a very weak function of state of charge. For example, accounting for the factor of  $\alpha$  in Fig. 4, the measured voltage at lower states of charge is relatively larger than the derivative line but the measured voltage at higher states of charge is relatively smaller than the derivative line. This implies that  $\alpha$  decreases slightly with increasing state of charge, indicating that the system has more energy losses at higher states of charge.

**Fig. 4** Comparison of the first derivative of strain (coupling factor) with parameters involved in energy harvesting, specifically peak voltage height. The shaded region represents error on the derivative curve. Y-error on the data points is due to standard deviation of multiple cycles and x-error is estimated from observed battery differences. The ranges and scales on the second axes are chosen to best align the data according to a proportional fit



Such a trend could be attributed to increased resistance of the battery at higher states of charge [18].

### Time Constant and State of Charge

In addition to the initial peak voltage strongly affecting the energy harvested, the time constant,  $b$ , will also affect the energy harvested (smaller values mean that the voltage decays more slowly and more energy is harvested). Building on equation (4), we will compare the experimental time constant,  $b$ , with the theoretical decay factor,  $\frac{2}{R_{ext}} \left( \frac{dV}{dQ} \right)_{SOC}$ . In particular, we will compare  $\left( \frac{dV}{dQ} \right)_{SOC}$  with  $b * R_{ext} / 2$ , where the resistance is nominally  $10 \Omega$ . Figure 5 depicts this comparison.

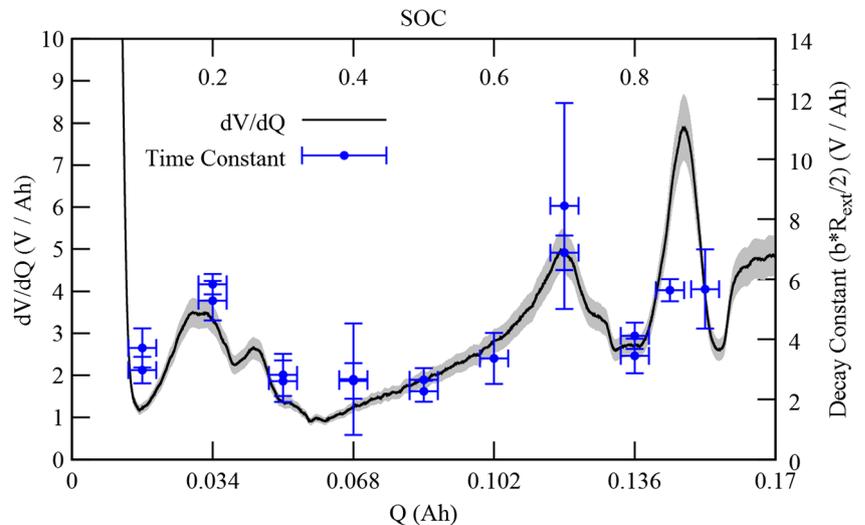
The trends in the measured decay constant matches the trend in  $dV/dQ$  very well. However, the measured decay constant is  $1.4 \pm 0.1$  times larger than expected, calculated via a

direct fit ( $bR_{ext}/2 = \beta \left( \frac{dV}{dQ} \right)_{SOC}$  where  $\beta = 1.4 \pm 0.1$ ). While  $\beta$  is essentially unity, this factor indicates that the real system decays to zero faster than the model predicts and is therefore less efficient than the model (i.e., there are unaccounted losses). This small factor could be due to the capacitive nature of the batteries not being exactly equal to  $dV/dQ$  or some other capacitive term that is not in the model. Overall, however, the comparison between  $dV/dQ$  and the measured time constant supports the model extremely well.

### Energy Efficiency

The true measure of success of an energy harvester is the amount of energy harvested. Lithium ion batteries do not generate significant amounts of energy (order nW of average power generation). However, this small amount of energy (order 1 mJ per hour) is useful for purposes such as wireless sensors

**Fig. 5** Comparison of measured adjusted decay constant and  $dV/dQ$ . The axes scales have been adjusted for best viewing. Y-error represents a standard deviation, x-error represents expected variation in maximum capacity, and the gray shading represents expected variation in the derivative from variation in maximum capacity



that require very small amounts of energy but are not easily accessible. Additionally, lithium ion batteries are not optimized intercalation materials and other materials and configurations could potentially produce orders of magnitude more energy. According to equation (7),  $\eta_{theory} = \frac{\alpha^2}{\beta} = 2.9 \pm 0.5\%$ . This theoretical efficiency is a constant for our system because  $\alpha$  and  $\beta$  are constants.

While this calculation represents the amount of energy harvested compared to what we would expect to harvest according to our model, in practice the total efficiency of the system also has viscoelastic terms from the compression and release of the battery. From Fig. 2, we calculated that  $\eta_{measured} = 0.012 \pm 0.004\%$ . This is significantly less than the  $\eta_{theory} = 2.9 \pm 0.5\%$ . This difference is due to battery materials such as the polymer separator. Essentially, regardless of energy dissipation over the load, compressing and releasing the battery will always result in a significant energy loss from the viscoelasticity of the battery components.  $\eta_{theory}$  is the maximum theoretical efficiency of our harvesting system that assumes no viscoelastic losses and assumes that the input work comes solely from movement of the applied force due to change in battery expansion when current flows. The  $\eta_{theory}$  is a reasonable maximum theoretical efficiency for a graphite and LCO battery system, and other similar systems likely have comparable efficiencies.

## Conclusion

Lithium ion batteries are extremely important for a clean energy future and remain one of the best commercial energy storage devices. In this work, we investigated lithium ion battery materials as mechanical energy harvesters and demonstrated that they can successfully be used to convert from mechanical to electrochemical energy in addition to storing energy. We characterized this process using basic circuit elements and provided a model and framework to predict the relevant energy harvesting parameters such as peak voltage and efficiency from basic mechanical and electrochemical data. While our commercial lithium ion batteries are not ideal energy harvesters, they serve well as a prototype for our model and demonstrate how our model can take raw expansion and voltage data from intercalation materials and predict energy production. From our model, we determined that the maximum theoretical efficiency for energy harvesting using these battery materials is  $2.9 \pm 0.5\%$ . Other similar systems will likely have a comparable maximum theoretical efficiency. In the future, we can use this model to help predict the effectiveness of other intercalation materials for mechanical energy harvesting. We can also aim to reduce viscoelastic losses, such as those from the polymer separator, and improve the real efficiency of the system.

**Acknowledgements** The authors thank Sydney Hall for assistance with data collection. Funding provided through Princeton University and the Princeton University School of Engineering and Applied Science.

## References

- Ramadesigan V, Northrop PWC, De S et al (2012) Modeling and simulation of lithium-ion batteries from a systems engineering perspective. *J Electrochem Soc* 159:R31. doi:10.1149/2.018203jes
- Cannarella J, Leng CZ, Arnold CB (2014) On the coupling between stress and voltage in lithium-ion pouch cells 9115:91150K. doi:10.1117/12.2055152
- Muralidharan N, Carter R, Oakes L et al (2016) Strain engineering to modify the electrochemistry of energy storage electrodes. *Sci Rep* 6:27542. doi:10.1038/srep27542
- Jacques E, Lindbergh G, Zenkert D et al (2015) Piezo-electrochemical energy harvesting with lithium-intercalating carbon fibers. *ACS Appl Mater Interfaces* 7:13898–13904. doi:10.1021/acsami.5b02585
- Sheldon BW, Soni SK, Xiao X, Qi Y (2012) Stress contributions to solution thermodynamics in Li-Si alloys. *Electrochem Solid-State Lett* 15:A9. doi:10.1149/2.016201esl
- Sethuraman V a, Srinivasan V, Bower a F, Guduru PR (2010) *In situ* measurements of stress-potential coupling in Lithiated silicon. *J Electrochem Soc* 157:A1253–A1261. doi:10.1149/1.3489378
- Sethuraman V a, Chon MJ, Shimshak M et al (2010) *In situ* measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation. *J Power Sources* 195:5062–5066. doi:10.1016/j.jpowsour.2010.02.013
- Massey C, McKnight G, Barvosa-Carter W, Liu P (2005) Reversible work by electrochemical intercalation of graphitic materials 5759:322–330. doi: 10.1117/12.601491
- Xu S, Hansen BJ, Wang ZL (2010) Piezoelectric-nanowire-enabled power source for driving wireless microelectronics. *Nat Commun* 1:93. doi:10.1038/ncomms1098
- Wang ZL, Song J (2006) Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science* 312:242–246. doi:10.1126/science.1124005
- Qin Y, Wang X, Wang ZL (2008) Microfibre-nanowire hybrid structure for energy scavenging. *Nature* 451:809–813. doi:10.1038/nature06601
- Koka A, Sodano H a. (2014) A low-frequency energy harvester from Ultralong, vertically aligned BaTiO<sub>3</sub> nanowire arrays. *Adv Energy Mater* n/a-n/a. doi:10.1002/aenm.201301660
- Cannarella J, Arnold CB (2015) Toward low-frequency mechanical energy harvesting using energy-dense Piezoelectrochemical materials. *Adv Mater* n/a-n/a. doi:10.1002/adma.201502974
- Kim S, Choi SJ, Zhao K et al (2016) Electrochemically driven mechanical energy harvesting. *Nat Commun* 7:10146. doi:10.1038/ncomms10146
- Schiffer ZJ, Cannarella J, Arnold CB (2016) Strain derivatives for practical charge rate characterization of lithium ion electrodes. *J Electrochem Soc* 163:A427–A433. doi:10.1149/2.0091603jes
- Pharr M, Suo Z, Vlassak JJ (2013) Measurements of the fracture energy of lithiated silicon electrodes of li-ion batteries. *Nano Lett* 13:5570–5577. doi:10.1021/nl403197m
- Smith a J, Dahn JR (2012) Delta differential capacity analysis. *J Electrochem Soc* 159:A290. doi:10.1149/2.076203jes
- Cannarella J, Arnold CB (2013) Ion transport restriction in mechanically strained separator membranes. *J Power Sources* 226:149–155. doi:10.1016/j.jpowsour.2012.10.093