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# Green paper-based piezoelectronics for sensors and actuators

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ABSTRACT

We report a novel biodegradable piezoelectric composite fabricated from paper and the piezoelectric salt, sodium potassium tartrate tetrahydrate (Rochelle salt, which we term PiezoSalt). The piezoelectric composite is non-toxic and is fabricated free of environmentally harmful solvents by impregnating PiezoSalt into a paper matrix through the crystallization of a concentrated PiezoSalt brine solution. The composite exhibits an effective piezoelectric constant between 3 and 25 $pC\,N^{-1}$, dielectric constant of 7, mass density of 625 $kg\,m^{-3}$, and a Young's modulus between 7 and 8 GPa. When directly actuated, cm-scale cantilevers consisting of PiezoSalt paper produced clearly audible sound waves, illustrating one potential application. PiezoSalt paper composite provides a scalable, high throughput approach for biodegradable sensors and transducers with unsurpassed environmentally friendly processing.



## 1. Introduction

The proliferation of computers and personal electronics has not only lead to continued innovation in technology and design, but also the significantly decrease in product lifespan, faster obsolescence, and increased electronic waste (e-waste [1]). With the emergence of the Internet of Things (IOT); smart sensors, labels, and actuators are being integrated into common household objects. It is predicted that by 2025, internet nodes may reside in food packages, furniture, and paper documents [2]. The continued growth of short lifecycle electronics has led to a global concern of the management of electronic waste or e-waste that is both difficult to recycle and incorporates many different environmental contaminants such as lead, tin, mercury, and cadmium [3]. The growing concerns of e-waste are being addressed by the development of substrates, sensors and actuators from fully biodegradable materials such as polyvinyl alcohol [4], paper [5], polylactic acid [6], and electroactive paper [7]. Using such materials allows for the environmentally safe deployment of electronic sensors and communication nodes for the IOT. The advent of paper-based electronics has led to the realization of scalable, large area fabrication of many electronic devices such as transistors, light emitting diodes, and photovoltaic cells [8–10]. As a composite matrix material, paper has been used with piezoelectric fillers for strain sensing [11,12] and nanogenerators [13], whereas engineered electrically active cellulose is used as an intrinsically piezoelectric material for actuators [14], and even biodegradable audio speakers [15].

Sodium potassium tartrate tetrahydrate, $NaKC_4H_4O_6{\cdot}4H_2O$, also known as Rochelle salt, was one of the first-known materials to exhibit ferroelectricity [16]. Unlike more widely-used piezoelectric materials such as lead zirconate titanate (commonly called PZT), Rochelle salt is water soluble and does not contain toxic elements. The Environmental Protection Agency classifies Rochelle salt as non-toxic. It is an approved food additive by the Food and Drug Administration [17], usually referred to as cream of tartar.

Rochelle salt has high piezoelectric constants with a reported maximum piezoelectric tensor constant $d_{14}$ of 2300 $pC\,N^{-1}$ [18–20]. Other crystallographic directions have piezoelectric coefficients of 27 and 430 $pC\,N^{-1}$ [18]. Therefore a single crystal has to be properly oriented maximize its piezoelectric properties [18]. These values are of the same order of magnitude as well-known ceramics. However, the lack of distinct orthogonal $d_{33}$ and $d_{31}$ piezoelectric constants and piezoelectric properties reported only up to 45 °C [18] make the use and engineering of this material challenging. Rochelle salt was used in microphones [21] and sensors [22] during the 1940's. The commercial use of Rochelle salt has since been eclipsed by the development of ceramic piezoelectric materials such as lead zirconate titanate (PZT) with its higher Curie temperature. However, the emerging field of low environmental impact technologies or *cleantech* [23,24] provides the impetus to investigate this once widely used material.

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We report here on the development of fully biodegradable PiezoSalt composites. The piezoelectric and mechanical properties of the Rochelle salt/paper composite are described. The fabrication and characterization of piezoelectric sensor and actuator components are reported.

## 2. Realization of Rochelle salt paper composite structures

### 2.1. Piezoelectric validation with pristine Rochelle salt crystal

In order to validate the piezoelectric properties of Rochelle salt, we used pure millimeter sized crystals as a piezoelectric actuator of a paper-based cantilever (Fig. 1). A Driving voltage is applied to the crystal, while the cantilever displacement was measured using a laser vibrometer. The first dynamic resonant mode of a paper cantilever had an out-of-plane amplitude higher than 200 pm. A decreasing phase from 0 to −180° indicates that the out-of-plane displacement is a consequence of the driving signal applied to the crystal. From this actuation, audible acoustic waves produced by the crystal could be heard. Several cantilever geometries were cut-out from paper sheet, the one characterized in Fig. 1b and c has the following dimensions: length of 8 mm, width of 1 mm, and thickness of 250 mm.

When considering fabrication, and the material resources involved, the above described micro-actuator concept is advantageous terms of its limited environmental impact. In order to leverage the potential utility of fully biodegradable piezoelectric material, composites comprising of a paper matrix and PiezoSalt filler was deemed a configuration that expands the application of piezoelectric Rochelle salt, without compromising biodegradability.

### 2.2. Composite preparation

Piezoelectric composites were synthesized by the impregnation of Rochelle brine solution into a paper matrix via capillarity. A saturated salt brine was prepared at a concentration of 630 g $L^{-1}$. Strips of paper were immersed into the saturated solution and the water was allowed to evaporate, the resulting composite can be seen in Fig. 2. Composite samples with electrodes were fabricated by first screen printing DuPont 5064H silver ink on top and bottom sides of pristine paper followed by curing for 30 min at 120 °C, electrode thicknesses were between 5 and 8 μm. These silver electrodes are not environmentally friendly and neither biodegradable. Nevertheless, screen printing allows a good electrical contact between the Rochelle salt and the electrode, thus was deemed suitable for this study. Other deposition techniques and conductive materials could also be used (gold, or biodegradable metals such as iron or magnesium [25]). After electrode deposition, Rochelle salt in liquid phase is loaded into paper by capillarity, the dried impregnated paper is shown in Fig. 2b.

### 2.3. Composite microstructure

Micrographs show the initial blank paper with a random arrangement of paper fibers in Fig. 3a. After PiezoSalt impregnation, the polycrystalline structure within the fiber network is clearly visible in Fig. 3b. With the inner structure of paper fiber unchanged, the polycrystalline Rochelle salt surrounds the paper fiber network. While the initial thickness of pristine paper is 250 μm, cross-section micrographs (Fig. 4) of impregnated paper and electrodes reveal a thickness of 400 μm. The expansion is thought to occur from the formation of air-filled cavities (i.e., larger porosity) within the paper matrix due to slow water evaporation and salt crystallization. The cross-section micrograph of Fig. 4d reveals the polycrystalline structure of the salt impregnated inside the paper and in between the silver electrodes. This confirms that the Rochelle salt migrated

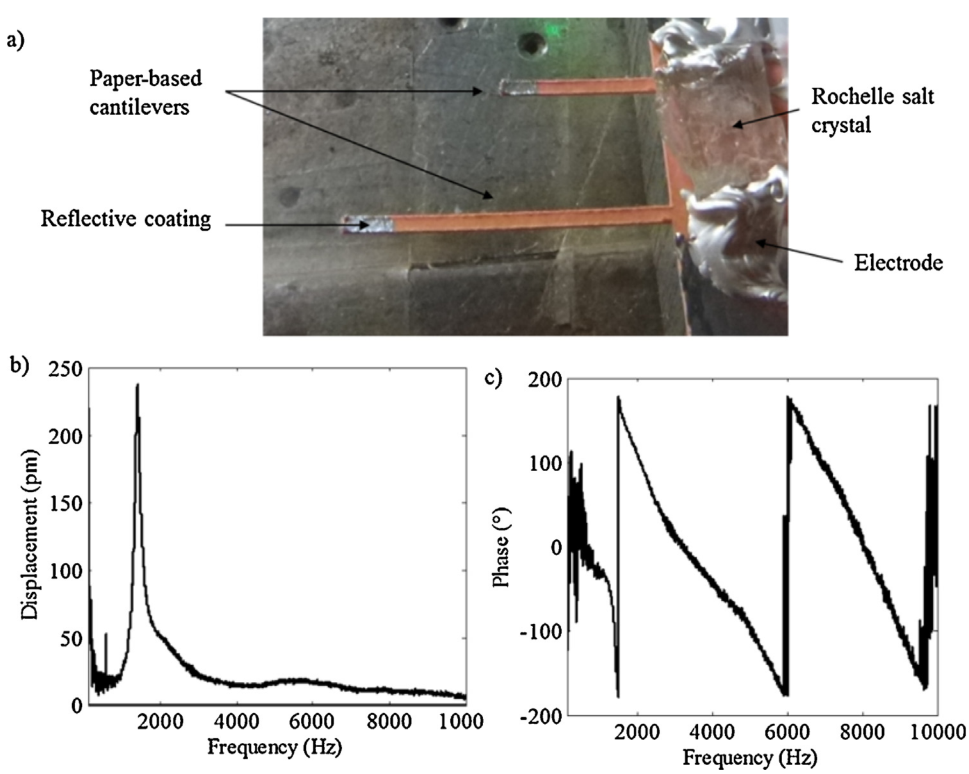


**Fig. 1.** (a) Array of paper cantilevers of several lengths actuated by acoustic waves produced by a Rochelle crystal fixed on the paper sheet. (b) Module and (c) Phase of the displacement of a cantilever.

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