Zn/Cu-vegetative batteries, bioelectrical characterizations, and primary cost analyses

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Developing a cheap, sustainable, and simple to use low power electrical energy source will substantially improve the life quality of 1.6×10^9 people, comprising 32% of the developing non-Organization for Economic Co-Operation and Development populations currently lacking access to electrical infrastructure (World Energy Outlook, 2006, http://www.worldenergyoutlook.org/2006.asp, 10 September 2009). Such a source will provide important needs as lighting, telecommunication, and information transfer. Our previous studies on Zn/Cu electrolysis in animal tissues revealed a new fundamental bioelectrical property: the galvanic apparent internal impedance (GAII) [A. Golberg, H. D. Rabinowitch, and B. Rubinsky, Biochem. Biophys. Res. Commun. **389**, 168 (2009)], with potential use for tissue typing. We now report on new fundamental studies on GAII in vegetative matter and on a simple way for significant performance improvement of Zn/Cu-vegetative battery. We show that boiled or irreversible electroporated potato tissues with disrupted cell membranes generate electric power up to tenfold higher than equal galvanic cell made of untreated potato. The study brought about basic engineering data that make possible a systematic design of a Zn/Cu-potato electrolytic battery. The ability to produce and utilize low power electricity was demonstrated by the construction of a light-emitting diode based system powered by potato cells. Primary cost analyses showed that treated Zn/Cu-potato battery generates portable energy at ~9 USD/kW h, which is 50-fold cheaper than the currently available 1.5 V AA alkaline cell (retail) or D cells (~49–84 USD/kW h). Admittedly very simple, the treated potato or similarly treated other plant tissues could provide an immediate, environmental friendly, and inexpensive solution to many of the low power energy needs in areas of the world lacking access to electrical infrastructure. [doi:10.1063/1.3427222]

I. INTRODUCTION

Over 2 centuries ago, Galvani initiated a pioneering research on the electrical properties of biological tissues.[1] Inspired by those "animal electricity" experiments, Volta invented "a device capable of producing electricity by the mere contact of conducting substances of different species."[2] The invention of "Voltaic battery" had marked the birth of a new era in the development of modern physics and made a significant change in our lifestyle.[3]

Battery technology evolved over the years from the one dependent on biological matters solely to a more efficient inorganic-reactions-based technology on one hand and the development

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of advanced organic galvanic batteries for medical applications on the other.[4,5] From the 1980s onward, however, the latter was mostly abandoned with the exception of some basic school experiments.[6] Recently, the use of either biological fluids or tissues' metabolic processes for power generation is gaining a new interest[7–9] mainly for the development of organic fuel cells.[8,9]

Revisiting the basic performance of organic galvanic cells, we have taken a different approach and studied the Zn/Cu electrolysis in animal tissues as a means for generation of internal electricity for powering both microrobots and/or implanted medical devices.[10] Our study revealed a new fundamental and measurable tissue-specific property—the galvanic apparent internal impedance (GAII),[10] a trait related to both the salt bridge function of a given tissue delineated between electrodes and to the "battery internal resistance" properties.[10,12] The discovery of GAII opens the way to the development of novel implantable self-powered and self-calibrated tissue diagnostic systems.[10]

Using the tools and principles of modern battery research,[12] we hereby report on further characterization of GAII in vegetative matter (potato) including the basic response patterns of the Zn/Cu-potato galvanic cell, the discharge properties, GAII, AC impedance, battery capacity, and energy production cost. Our results clearly show that an irreversible change in the cellular and tissue structures either through irreversible electroporation or boiling significantly affects GAII values with the consequent order of magnitude increase in the power generated by the vegetative cell. The increased power output has an immediate relevance to many electrically powered applications and especially to the economically disadvantaged communities by providing cheap and easy to use access to the latest breakthroughs in photonics and solid state lightening,[13,14] communication devices, computers, and more.

II. MATERIALS AND METHODS

A. Battery design

The Dutch bred potato (*Solanum tuberosum*) cv. "Desiree"—the world's most popular red skinned yellow flesh main crop potato[11]—was used throughout. The mineral composition of the potato used is given in Table I. We compared electrical energy output from cells made of potato tubers treated as follows: (a) fresh, (b) irreversibly electroporated,[15] and (c) boiled.

For electrolytic studies the analyzed tissues made of a single potato slice were sandwiched between Zn and Cu flat parallel electrodes with various surface areas separated by a 29 ± 1 mm gap (Fig. 1) and discharged using an external load.

B. Electrical properties measurements

The performance of the vegetative battery was evaluated using a computer controlled electrochemical analyzer (CH 680, CH Instruments, Inc., Austin TX, USA). The battery properties, e.g., current profile, capacity, and energy, were measured by discharging over a constant 300 Ω external resistance for 20 h. The external load voltage was measured at 1 Hz frequency. GAII was calculated from discharging data obtained by the Zn/Cu-potato galvanic cell using a range of 2.5–100 000 Ω electrical resistances. AC impedance spectroscopy in the range of 10 Hz and 1–100 kHz was performed by sandwiching a potato slice between two Al electrodes. In all experiments, the entire air-exposed surface of the potato tissue was covered with Parafilm® (Alcan Packing WI, USA) to reduce drying and oxidation. Five replications were employed throughout.

C. Cell membrane treatment by irreversible electroporation

The role of cell membranes during the electrolytic process was determined by comparing the power generated by untreated potato tissue with that of nonthermal irreversible electroporated potatoes. The latter cell membranes were impaired, but other organic and inorganic components remained intact.[15] Nonthermal irreversible electroporation was performed by sandwiching potato slices between two Al electrodes connected to an electroporator power supply (BTX 830, Harvard Apparatus, Holliston, MA). Ten unipolar 100 μs long, 400 V/cm rectangular electrical pulses

TABLE I. Potato content analyses by ion chromatography and atomic emission spectroscopy.

Substance	Concentration(mg/l)
NO_3^-	1.4
PO_4^{-3}	975
SO_4^{-2}	77
Ag	<0.0025
Al	4.7
As	<0.025
B	1.37
Ba	0.043
Ca	153
Cd	<0.0025
Co	0.043
Cr	0.025
Cu	2.75
Fe	4.35
Hg	<0.003
K	4900
Li	0.09
Mg	332
Mn	2.08
Mo	0.087
Na	165
Ni	0.25
P	563
Pb	<0.025
S	363
Sb	<0.005
Se	<0.005
Si	12
Sn	0.050
Sr	0.212
Ti	0.088
V	0.017
Zn	5.25

were delivered at 5 Hz to induce irreversible electroporation without thermal effects. The effects of heating on organic tissues during irreversible electroporation were discussed in our group's previous works.[16]

D. Organic molecules denaturation by boiling

With the exception of cell membranes, the irreversible electroporated potato intact tissue[15] represents a solid organic medium. Additionally, we evaluated the general role of other organic components on the electrolytic process. To this end we compared the cells' properties made of untreated potatoes with those of both irreversible electroporated and boiled potato tissues. For scientific rigor, fresh sliced potatoes were immersed in a 4.9 g/l KCl solution and microwaved (Cristal WP900AP23 microwave oven, Cristal Machinery, Ltd., China) at 810 W for 5 min.[17,18]

E. Potato mineral composition

Homogenates of fresh potatoes were squeezed through a filtering pad (Padssan Gauze Pad Lot No. 3233) and, following 10 min small particles' precipitation, were refiltered using a BD Falcon™ Cell Strainer (40 μm Nylon REF 352340 BD Bioscience, Bedford, MA, USA). Thereafter,

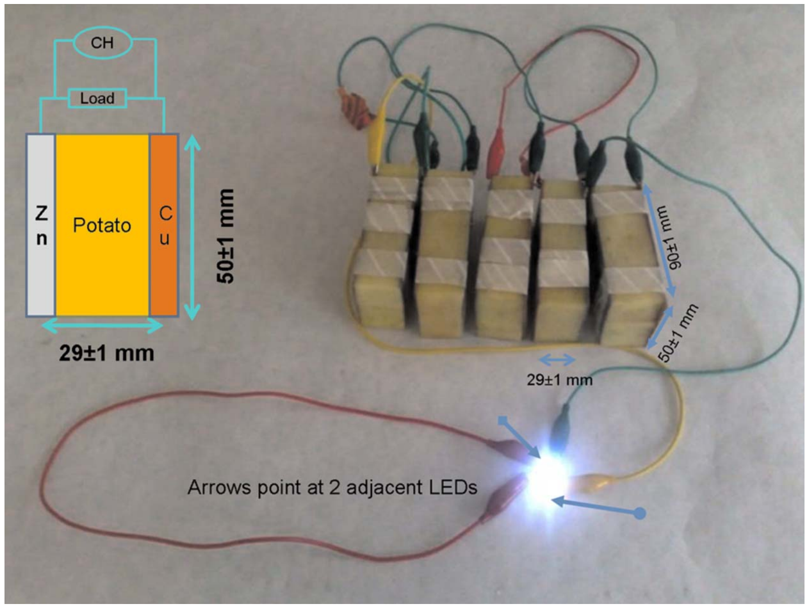

FIG. 1. Potato battery basic composition and performance. Potato Zn/Cu galvanic cell battery basic structure. The battery (K_{cell}=15.5 cm) was used to light two white LEDs.

the filtrates were twice filtered through 0.2 μm reverse phase filter and subsequently analyzed for nitrate, phosphate, and sulfate using ion chromatograph (ICS 300, Dionex, CA, USA). For trace elements analysis (atomic emission spectroscopy, ICP ARCOS, Spectro, Inc., Germany), 2 ml 65% nitric acid were added to 10 ml microwaved potato filtrate, and a final volume of 25 ml was obtained by adding de-ionized water (Table I).

III. RESULTS AND DISCUSSION

A. Battery discharge characterization

Current density profiles of three tested biogalvanic cells, discharged over 300 Ω constant external resistance and monitored during 20 h, are shown in Fig. 2(a). A typical current density/time signature generated by a battery made of an untreated potato tissue with K_{cell}=5.5 cm presents a rough estimate of the time required for transient phenomena such as the development of diffusion layer near the electrodes to occur [Fig. 2(a)]. Cell constants K_{cell} (cm) are defined as the surface area of an electrode over distance between electrodes.

Systematic electrochemical analyses were performed by discharging electrodes of different surface areas over a range of electrical resistances [Fig. 2(b)]. It is evident that the current density during the discharge from a battery made of untreated potato as a function of voltage measured between the electrodes is inversely related to the cell constant (surface area of the electrodes in our particular setup). Maximum voltage output from this battery at zero load is about 0.76 V.

Figure 2(c) shows in ascending order the voltage produced by batteries made of untreated potatoes, irreversible electroporated potato, and boiled potato as a function of the external resistance across the electrodes. It is evident that the latter two generate significantly higher voltage and higher currents [Fig. 2(d)] than fresh tubers' batteries. The difference may reach one order of magnitude at lower potential differences, i.e., low external loads.

Figures 2(b)–2(d) show that open circuit voltage (OCV) or electromotive force of the potato battery at zero current is about 0.76 V, a potential consistent with a Zn electrolytic value in relation to a hydrogen electrode.[19] It ranges from 0.65 V probably due to electrode passivation to 0.89 that

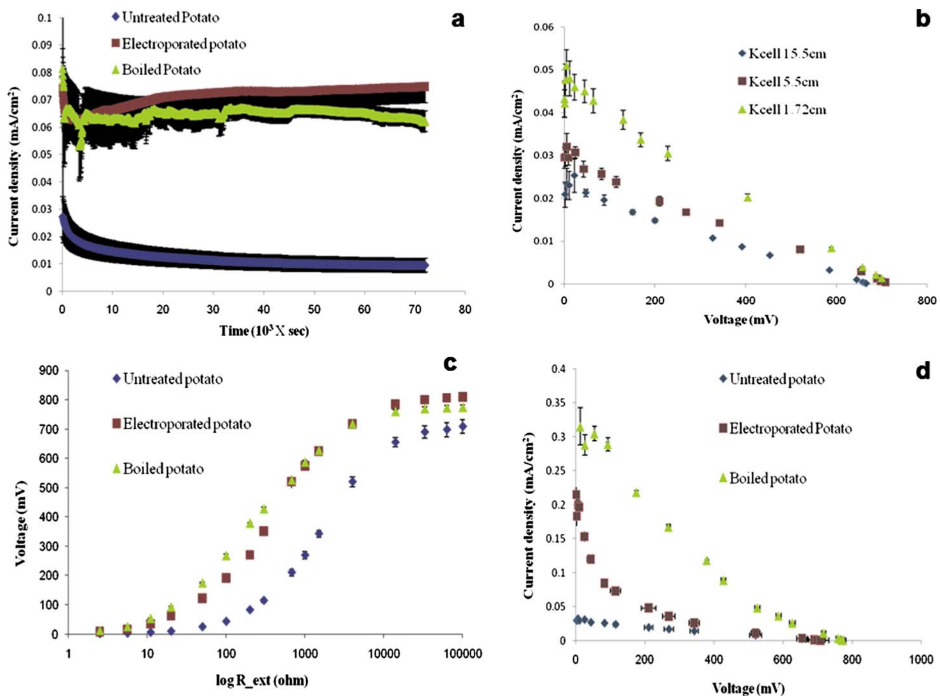

FIG. 2. Zn/Cu battery electrical discharge characteristics. (a) Battery (K_{cell}=5.5 cm) characteristic performance during 20 h discharge through a constant 300 Ω external resistance. (b) The effect of cell constant K_{cell} on the performance of an untreated potato battery. (c) Effect of physical disruption of potato tissues on the battery voltage as a function of external resistance between the electrodes. (K_{cell}=5.5 cm). (d) Effect of physical disruption treatments of potato tuber on the relation between battery output voltage and current density performance (K_{cell}=5.5 cm). Error bars—one standard deviation, n=5.

could be explained by reactions of unknown nature occurring on the electrodes' surface. Our results suggest that the Zn electrode and the reduction of hydrogen at the Cu electrode are the dominating reactions,[19] as depicted in Eq. (1),

$$\text{on Zn:Zn} \rightarrow Zn^{++} + 2e^-, \quad E^0 = 0.76 \text{ V},$$

$$\text{on Cu:}2H^+ + 2e^- \rightarrow H_{2,} \quad E^0 = 0 \text{ V} \tag{1}$$

$$:Zn + 2H^+ \rightarrow Zn^{++} + H_2, \quad \Delta E^0 = 0.76 \text{ V}.$$

We conclude that the primary mechanism of energy production by the Zn/Cu-potato battery is electrolysis and that potato tissues connected to Cu and Zn electrodes function as a typical KCl salt bridge (albeit solid). The nature of this bridge impedance seems to dominate the performance of the plant tissue battery [Fig. 2(d)], which is also the case in commercial inorganic batteries.[12] In fact a major challenge in inorganic battery design is the minimization of the battery internal impedance.[12]

B. GAII and AC impedance analyses

Based on the information obtained on the relationship between current density and voltage [Figs. 2(b)–2(d)], battery design techniques[12] can be applied for devising plant tissue based batteries. The proposed potato galvanic cell can thus be used as a voltage source with an open circuit voltage in series with galvanic apparent internal resistance R_{app}. The value of the latter can be estimated from I_d circuit current measurements [Eq. (2)] where GAII represents the combined value of R_{app} and cell geometry,[12]

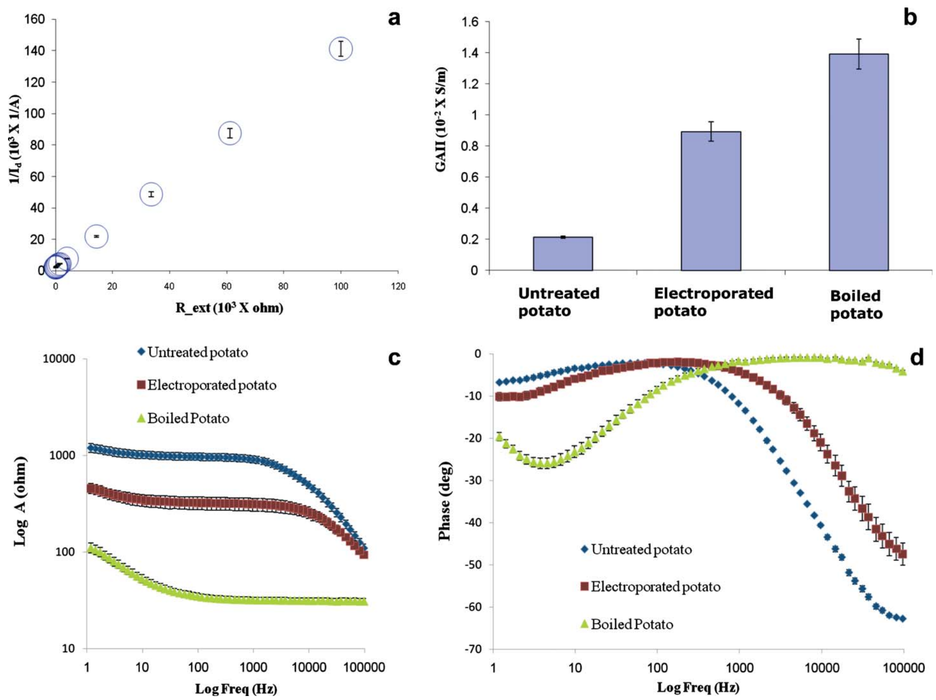

FIG. 3. Characterization of potato GAII and AC impedance. (a) A typical plot of $1/I_d$ as a function of external resistance for an untreated potato. (b) GAII of the salt bridge calculated after 3 h of discharge. [(c) and (d)] The real impedance of the potato. They represent two parts of a standard Bode plot of electrical impedance ($K_{cell}=5.5$ cm). Error bars—one standard deviation, n=5.

$$\frac{1}{I_d} = \frac{R_{ext}}{OCV} + \frac{R_{app}}{OCV},$$

$$GAII = \frac{1}{R_{app}A}\left(\frac{S}{cm}\right). \tag{2}$$

Plotting $1/I_d$ against R_{ext} [Fig. 3(a)] shows a highly linear performance, thus supporting our hypothesis that the potato battery reacts as an Ohmic resistance over a wide range of external loads. This linear response allows a good estimate of GAII, which reflects the conductance of the salt bridge between the electrodes during the electrolytic process.

Equation (2) and the data in Fig. 2(c) were used for calculating the GAII in batteries made of potato tissues submitted to destructive treatments [Fig. 3(b)]. Untreated and boiled potatoes had the lowest and highest values, respectively, and electroporated potatoes were intermediate.

Spectroscopic measurements of the complex impedance in a wide range of frequencies are commonly used for organic matter characterization.[20] Hence, untreated potatoes' cells show a typical electrical behavior of intact organic matter[20] with alpha and beta dispersions with frequency ranges of about 10 Hz and 1–100 kHz, respectively [Figs. 3(c) and 3(d)]. The alpha and beta dispersion types relate to the composition of the electrolytes' solution and to the integrity of cell membranes, respectively. The spectroscopic signature of electroporated potato shows only a residual beta dispersion, thus indicating a residual presence of cell membranes, whereas that of boiled potatoes shows no beta dispersion due to total destruction of cell membranes.

C. Battery capacity

When the data in Fig. 4 are combined with those in Figs. 2 and 3, a better insight into the potato battery system is gained, thus allowing for optimization of vegetative battery design. Trans-

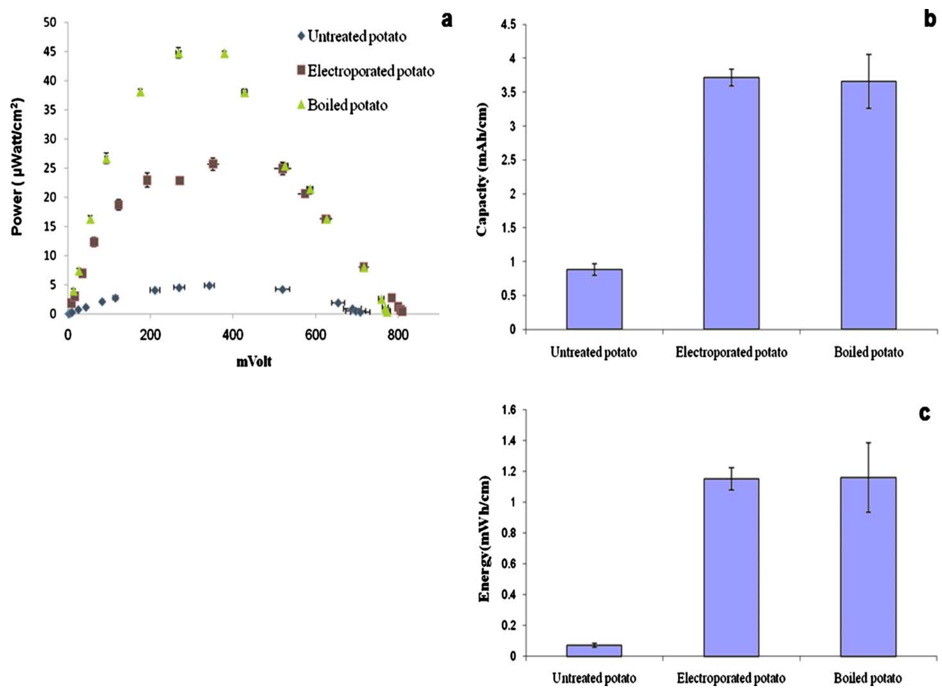

FIG. 4. Energy production by a potato battery. (a) Battery power generation per cm^2 working electrode as a function of the battery voltage. (b) Battery capacity throughout 20 h discharge over constant external resistance (300 Ω). (c) Total energy produced by a potato battery during the 20 h (battery discharge occurred over constant external resistance of 300 Ω (K_{cell}=5.5 cm). Error bars—one standard deviation $n=5$.

formation of the data in Fig. 2(d) shows the power delivered by the potato battery per unit electrode surface area as a function of output voltage [Fig. 4(a)]. The figure also shows that maximum power is delivered only at a certain voltage and that lower values are generated at above and below the optimal voltage. Maximal power delivered by boiled potato cells with ruptured cell membranes may reach values an order of magnitude higher than that generated by untreated potato. When compared with the data in Fig. 3(b), a direct relationship between the ability of the vegetative battery to deliver power and GAII becomes evident. The significant increase in electrical energy generation with membrane destruction led us to propose that ionic diffusivity through the tissue bridge between electrodes is the *raison d'etre* of this phenomenon, as effective diffusivity of protons increases with membrane rupture. In contrast, the rate of proton flux is reduced when cell membranes are intact probably due to the tortuosity of the extracellular space as well as the equivalent reduction in the concentration of electrolytes per unit volume when the intracellular fluids do not actively participate in the ionic transport.

The potato battery was further characterized. Battery capacity (C) is defined as the amount of ampere∗hour (A∗h) that can be drawn from the cell [Eq. (3)] under specified conditions of temperature, rate of discharge, and final battery voltage,[12]

$$C = \int_0^t I(t)dt \ \ (A\ h), \tag{3}$$

where the discharging current I(t) depends on the external resistance as in Eq. (2).

The amount of energy (E) in watt∗hour (W h) that can be drawn from the battery is given by the voltage between the electrodes V(t) and the current I(t) [Eq. (4)],

$$E = \int_0^t V(t)I(t)dt \ \ (W\ h), \tag{4}$$

where for a constant electrical discharge through an external electrical resistance, the relation between energy and discharging current is depicted in Eq. (5),[12]

$$E = \frac{1}{R}\int_0^t V^2(t)dt(W\ h). \tag{5}$$

The graphs in Figs. 4(b) and 4(c) were calculated from data collected along 20 h experiments [Fig. 2(a)]. These graphs describe both potato cell's capacity and energy availability. When averaged over 20 h, the energy generating capabilities of cells made of microwaved and electroporated potatoes were similar but significantly higher from those delivered by batteries made of fresh tubers.

D. Primary energy cost analyses

A 20 h power discharge from potato cells with 29 ± 1 mm distance between 16 cm^2 Zn and Cu electrodes' surface areas, across a 300 Ω resistance [Fig. 2(a)], showed that at maximal performance the treated Zn/Cu-potato cell is markedly more economical than a typical 1.5 V AA alkaline or D batteries.

For economic analyses we compared the price of a standard Energizer E91 1.5 V AA alkaline cell retailed at 1.89 USD/battery[21] and of D cells mostly used in rural areas[22] with that of Zn/Cu-potato cells.

The Energizer manufacturer's data sheet[23] specifies the cell's maximum capacity of 2.8 A h. Thus its total energy contents amounts to $(2.8\ \ A\ h^{*}1.5\ \ V)$ 4.2 W h, and the retail energy price of this specific battery equals to 450 USD/kWh. In Nicaragua, 45% of the population lives in rural areas where monthly income ranges between 26 and 250 USD and power supply reaches only ~25% of the households.[22] Others meet their electricity needs with disposable batteries, paying 49–84 USD/kWh for the power they use for off grid communication and lighting.[22]

In comparison we calculated the costs of energy produced by a Zn/Cu-potato cell. The calculations are based Faradays' laws[24] [Eq. (6)] for Zn, and our measurements of currents over time [Figs. 2(a) and 4(c)],

$$m\left(\frac{g}{cm}\right) = \frac{M\left(\frac{g}{mol}\right)\frac{It}{cm}\left(\frac{Ah}{cm}\right)}{n\left(\frac{mol}{equiv}\right)F\left(\frac{Ah}{equiv}\right)}, \tag{6}$$

where m is the mass of consumed metal normalized by the cell constant.

Further calculation [Eq. (7)] reveals the Zn consumption for boiled potato cell over a 20 h discharge period,

$$m = \frac{65.38\frac{g}{mol} * 3.66\frac{mAh}{cm}}{2\frac{mol}{equiv} * 26.8\frac{Ah}{equiv}} = 4.47\frac{mg}{cm}. \tag{7}$$

Normalizing Zn consumption to electrode surface area (dividing by 2.9 cm) and for total operation time (20 h) resulted in a mean value of 77 $\mu gZn\ cm^{-2}\ h^{-1}$ consumption rate at electrode surface.

The calculated cost of energy production by potato cell is thus described in Eq. (8),

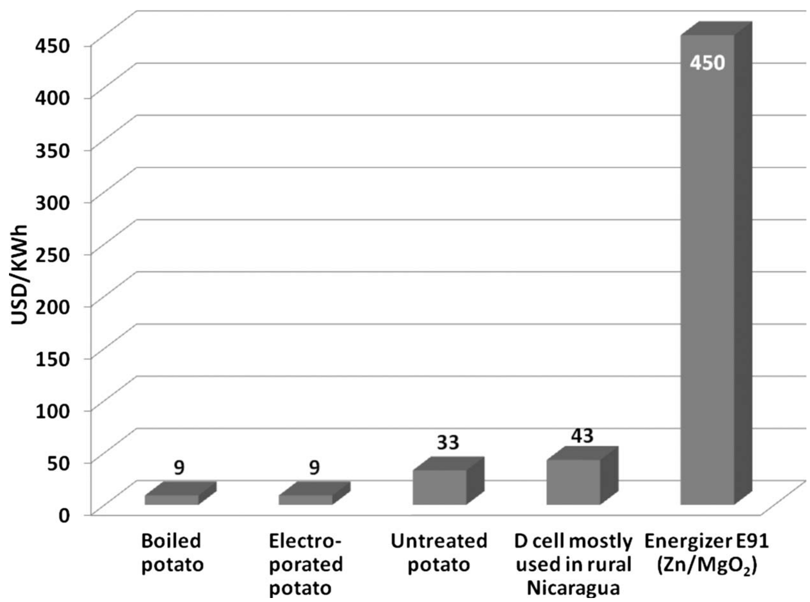

FIG. 5. Cost analyses comparison between various portable battery sources.

$$\mathrm{cost}\left(\frac{\mathrm{USD}}{\mathrm{kW\ h}}\right) = \frac{\mathrm{cost}\left(\frac{\mathrm{USD}}{\mathrm{cm}}\right)}{\mathrm{energy}\left(\frac{\mathrm{mW\ h}}{\mathrm{cm}}\right)} * 10^6\left(\frac{\mathrm{mW\ h}}{\mathrm{kW\ h}}\right), \tag{8}$$

where cost (USD/cm) is calculated by multiplying the mass (mg cm^{-1}) obtained in Eq. (7) by cost (USD kg^{-1}) and energy [Fig. 4(c)] is calculated from our measurements of currents over time [Fig. 2(a)].

At 2.22 USD Zn kg^{-1} (London Metal Exchange, 22/11/2009) and excluding the marginal costs of boiling and the potato slice and Cu electrode (not consumed), we estimate the energy cost of boiled potato Zn/Cu-battery at ~9 USD/kW h. Figure 5 compares the costs of various portable batteries sources.

E. Lighting application

The potential of this simple technology to respond to low power electrical energy needs is demonstrated in Fig. 1. Two white standard light-emitting diodes (LEDs), requiring a minimum forward current of 2 mA and a voltage of 1.8 V, were connected in parallel to five boiled potato cells, each with 45 cm^2 working area. In this case the LED emitted a continuous light for 3 h until voluntarily disconnected.

Mills *et al.* reported that in developing countries, LEDs consuming 8.3–53.1 lm/W are available for off grid lighting[14,25] and that kerosene lantern efficiency is 0.08–0.11 lm/W.[25] Providing energy for LED by the Zn/Cu-boiled potato cell is expected to cost 0.16–1 USD/1000 lmh. Comparing it to various kerosene lamps, which produce light at 3.69–5.81 USD/1000 lmh,[14] it is obvious that using the former for lighting can increase power availability to people in undeveloped areas. Boiling is affordable all over; hence our technology may be implemented instantly for lighting and also for other applications including communication (portable radio and cellular phones), computers, simple medical equipment, and more.

F. Design considerations

Potato has been selected for this design due to its popularity and availability worldwide. After maize, wheat, and rice, potato is the world's fourth most important food crop with an annual production of more than 323×10^6 tons (Ref. 26) with more than one-third coming from developing countries, up from just 11% in the early 1960s.[27,28] Potatoes are produced in 130 countries over a wide range of climates, from temperate zone to the subtropics—more than any other crop worldwide but corn.

For easy application, user convenience and friendly design are important factors of batteries' technology, as much as the electrochemical design and battery performance. The designer of the proposed battery should take into consideration the prevailing conditions in the target areas. As discussed above, the choice of potato tubers is based on its popularity worldwide.[26] Second, liquid cells are being replaced by solid state batteries due to the robustness and convenience of latter.

The simple design proposed in Fig. 1 requires no additional components to the Zn and Cu electrodes; it requires no corrosive-resistant fluid chamber and no preparation and calibration of electrolytic solution; and it is cheap and requires no special skills for assembly. Hence potato cells provide an abundant and renewable source of cheap and elegant solution to the needs of people in regions free of central power supply. Boiling further increases efficiency and facilitates the reduction in the internal impedance of the salt bridge. We thus propose that such a device can easily be adopted by those lacking electrical infrastructure as part of the daily routine.

IV. CONCLUSIONS

The bioelectrolytic low power electrical energy source introduced in this study brings an extra dimension to the utilization of the globally fourth most abundant crop, accessible essentially all over the world, made of solid components, and requires low initial financial investment compared with solar or conventional batteries. Boiling and the simple assembly do not require special skills; it is both easy to operate and environment friendly. Last but not least, the power generated by Zn/Cu-potato is much cheaper than any conventional portable battery and produces with LED's substantially cheaper lighting than kerosene. The proposed technology may be immediately implemented in the developing countries for improving the life quality on numerous people who do not have access to grid electricity.

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