Photoferroelectric solar to electrical conversion

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We propose a charge pump which converts solar energy into DC electricity. It is based on cyclic changes in the spontaneous electric polarization of a photoferroelectric material, which allows a transfer of charge from a low to a high voltage. To estimate the power efficiency we use a photoferroelectric liquid crystal as the working substance. For a specific choice of material, an efficiency of 2% is obtained.

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Photoferroelectrics are materials in which their ferroelectricity can be affected by exposure to light. We propose a device that works as a charge pump based on the photoferroelectric effect. Varying light intensity cycles a photoferroelectric working material through various electric polarization states and the associated charge in the external circuit is pumped from low to high potential.

A body with a uniform (ferroelectric) polarization $P_s^0$ has zero polarization charge density in the bulk, $\rho_{\text{pol}} = \nabla \cdot P_s^0 = 0$, while the surface charge density associated with the change of polarization from its finite bulk value to zero on traversing the surface cutting $P_s^0$ is given by $\sigma_{\text{pol}} = P^0_s$. Figure 1 shows this $\sigma_{\text{pol}}$ associated with truncating $P_s^0$. Such a layer of charge $\sigma_{\text{pol}}$ creates an internal electric field $E_s^0 = -P^0_s/\varepsilon_0$ in the material in this slab geometry, where $\varepsilon$ is the relative dielectric constant of the material. In the presence of the electrodes on the surfaces of the slab that are shorted together ($V_1 = 0$ in Fig. 1), and the absence of the insulating layers, external free charges of surface density $\sigma_f = -\sigma_{\text{pol}}$ flow to neutralize $\sigma_{\text{pol}}$. These free charges vitiate the field $E_s^0$ between the plates by creating an opposite field, $E_1$, that is in the direction of $P_s^0$. See Fig. 1 for counter charge layers $\pm \sigma_f$ on the bounding electrodes. In fact, they have been further adjusted from $\pm \sigma_{\text{pol}}$ in order to increase $E_1$ so that the net field matches the actual applied potential $V_1 \neq 0$ instead. It is such free, external balancing charges we aim to optically pump.

Considering the two electric fields, the voltage $V_1$ can be expressed in the form

$$V_1 = \int dx \left( E_1 - E_s^0 \right) = \sigma_f \left( \frac{2b}{\varepsilon_0 \varepsilon_1} + \frac{L}{\varepsilon_0 \varepsilon} \right) - \frac{P^0_s L}{\varepsilon_0 \varepsilon}, \quad (1)$$

where $L$ is the thickness of the photoferroelectric sample itself, $b$ is the thickness of insulating layers inserted between the sample and the electrodes to prevent charge flow, and $\varepsilon_1$ is the layers' relative dielectric constant. If $P_s^0$ were now diminished, then the internally-generated field $E_s^0$ would also be diminished. Now the field associated with the free, formerly partially neutralizing charges, if they cannot dissipate, generates an increased potential $V_{\text{on}} > V_1$ between the electrodes. This increased potential $V_{\text{on}}$ allows charge pumping.

The spontaneous polarization of a photoferroelectric usually decreases under light irradiation as photons are absorbed and modify the polar ordering. Since light is absorbed the beam is necessarily attenuated and the polarization profile can no longer be uniform (except when light is powerful enough that $P_s(x) = 0$ at all depths $x$). Then $\nabla \cdot P_s$ is non-zero also in the bulk, and polarization charges will emerge inside the sample as well as at the surface. Consequently a non-uniform electric field $E_s(x, t) = -P_s(x, t)/\varepsilon_0 \varepsilon$ appears in the sample, where $P_s(x, t)$ is the electric polarization at the point $x$ and the illumination time $t$; note that $E_s(x, t) \leq E_s^0$. As the diode prevents backflow of the charge to the battery (see Fig. 1), the resulting voltage $V_{\text{on}}(t)$ between the electrodes will be greater than $V_1$:

$$V_{\text{on}}(t) = \sigma_f \left( \frac{2b}{\varepsilon_0 \varepsilon_1} + \frac{L}{\varepsilon_0 \varepsilon} \right) - \frac{1}{\varepsilon_0 \varepsilon} \int_{-L/2}^{L/2} P_s(x, t) dx, \quad (2)$$

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FIG. 1. A slab of ferroelectric of thickness $L$ with two insulating layers of thickness $b$ under the bounding electrodes. A polarization surface charge layer $\sigma_{\text{pol}}$ associated with truncating the spontaneous polarization $P_s^0$ generates an internal field $E_s^0$. A free surface counter charge layer $\sigma_f$ partially neutralizes the polarization charges to give a resultant electric field commensurate with an applied voltage $V_1$. The electric field $E_1$ of charges $\sigma_f$ is also indicated.

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that the charge can flow from the voltage battery. Many different materials exhibit photoferroelectric behavior, and might be potential candidates for use in our device. We therefore explore the suitability of these materials for a charge pump, optimize their performance by specifying an appropriate electric circuit, and calculate the efficiency of such pumps. Our general analysis is applicable to all photoferroelectric materials. Only our final estimate of the efficiency of the pump will be demonstrated for particular substances, photoferroelectric liquid crystals.

The circuit diagram of the charge pump is shown in Fig. 2. The central component of this circuit is the photoferroelectric sample S placed between transparent conducting electrodes. The arrangement of diodes is such that the charge can flow from the voltage battery V1 to a higher voltage V2 only. We shall describe how the electric polarization varies during a cycle.

The photoferroelectric sample S in the dark state is connected to the voltage V1. When light is shone on the sample, the electric polarization decreases and the voltage across the electrodes is increased above the value V1, with charge on the electrodes being fixed (the left diode prevents backflow of charge). As the electric polarization further decreases, the voltage across the electrodes increases until it reaches the value V2. Then the charge starts to flow through the right diode, which leads to its being pumped into battery V2 at constant voltage (Fig. 2). If the connection of the sample with the battery V2 were absent, the voltage across the sample would rise to a value we simply denote by Von corresponding to Von(t) with t = ton, the duration of the illumination phase of the cycle.

The charge transferred to the battery V2 is equal to Δq = C(Von − V2), where C is the total capacitance of the sample. There are two insulating layers of capacitance Cb and a liquid crystal of capacitance Cl connected in series. The equivalent capacitance is given by 1/C = 2/Cb + 1/Cl = (2b/ε1 + L/ε)/ε0A), where A is the area of the electrode. Taking into account that b ≪ L, and typically ε = ε1, one gets a simple expression C = ε0εA/L.

Upon switching off the light, the spontaneous polarization will evolve to a new state. Here, we shall suppose that it recovers its initial dark state value; this, in particular, holds for a large class of photoferroelectric liquid crystals. As the polarization increases in time, for a constant value of the charge on the electrodes, the voltage across the sample starts to decrease from its value V2. When the voltage drops to V1, new charges will start to flow from the left battery to maintain the voltage V1 across the electrodes. Finally, the charge on the electrodes recovers its value at the beginning of the cycle. This cycle is reminiscent of an optical charge pump based on a capacitance that is optically variable. In practice, a self-priming circuit would avoid exhausting battery V1.

The same total charge Δq pumped into the battery V2 is supplied by V1 to the electrodes during recovery process. Thus, the work output W of this charge pump is W = Δq(V2 − V1) = ΔqV, which gives

\[ W = \varepsilon_0 \varepsilon A L \Delta V \left( \frac{L}{\varepsilon_0 L} (P_s^0 - P_s(t_{on})) - \Delta V \right). \]  

We can maximize this output with respect to the voltage difference ΔV. Using the condition dW/dΔV = 0, we get the optimal choice of voltage difference

\[ (V_2 - V_1)^{opt} = \frac{L}{2\varepsilon_0 L} (P_s^0 - P_s(t_{on})) = \frac{V_{on} - V_1}{2}. \]  

Since to pump charge we require the open circuit developed voltage to exceed that of the upper battery, that is V2 < V_{on}, or equivalently V2 - V1 < V_{on} - V_1, we see that the above choice of voltage difference is allowed. Thus, for given voltages V1 and V_{on}, the optimal V2 is

\[ V_2^{opt} = \frac{V_1 + V_{on}}{2}. \]  

The maximum output W_m is then

\[ W_m = \frac{AL}{4\varepsilon_0} (P_s^0 - P_s(t_{on}))^2. \]  

Output is therefore higher if the dark state polarization P_s^0 and the average value of the polarization profile P_s(t_{on}) in the illuminated state differ more, that is if much polarization as possible is lost. The work delivered depends on the volume AL of the working material.

If I_{sun} is the incident solar flux, and U_{in} is the energy input per unit volume of the sample required to transform the polarization state of the working material, then t_{on} is determined by energy balance I_{sun}A_{on} = U_{in}AL. The period of a cycle τ = t_{on} + t_{off} = U_{in}L/I_{sun} + t_{off} then follows. Here, t_{off} is the characteristic time for relaxation of polarization to its dark state value. The power efficiency is then η = W_m/(τ I_{sun}A).
For such a device the power efficiency is about a unit axial vector the long molecular axes are orientationally ordered, in the ordinary isotropic liquid state. In the simplest nematic phase (SmA), the molecules are organized as two-dimensional layers, with the nematic director \( \mathbf{n} \) being parallel to the normal \( \mathbf{k} \) of the layers. In the smectic C phase (SmC), \( \mathbf{n} \) is no longer parallel to \( \mathbf{k} \), but is tilted by an angle \( \theta \) with respect to \( \mathbf{k} \) (Fig. 3). The tilt angle \( \theta \) is a function of temperature \( T \). At a given \( T \), the director \( \mathbf{n} \) is located on the surface of a cone formed by \( \mathbf{k} \) with opening angle \( \theta(T) \).

A SmC liquid crystal composed of chiral molecules is referred to as a SmC* (Fig. 3). As pointed out by Meyer, the emergence of a (local) spontaneous electric polarization \( P_s \) in SmC* is allowed along \( \mathbf{k} \wedge \mathbf{n} \) since the plane of \( \mathbf{k} \) and \( \mathbf{n} \) is not a mirror plane. The spontaneous polarization is a function of the tilt angle \( \tilde{\theta} \) and \( P_s \propto \theta \) for small \( \theta \). When the temperature is increased and crosses a threshold value, the SmC* phase most often undergoes a second-order phase transition to the non-polar SmA* phase.

The spontaneous polarization of a SmC* phase doped with photosensitive molecules (for example, an azo or thioindigo dye) can be changed by light irradiation. Pure systems of dyes have also been used. Some dye molecules can make transitions from the linear (trans) ground state to the excited bent-shaped (cis) state by absorbing a photon. The cis state isomers can disrupt the SmC* ordering, which leads to a change of \( P_s \), whence the name photoferroelectric effect. If the interaction with light is sufficiently strong it can completely destroy the SmC* phase, causing a transition to the non-polar SmA* phase. Dye molecules in the excited cis state re-isomerize thermally back to the ground trans state with some characteristic time. Upon removal of light, the electric polarization eventually regains its initial dark state value.

Recently, it has been argued that the mechanism and details of light absorption are crucial to understanding the optical depression of electric polarization. Given that materials without substantial layer shrinkage have also been found, in our simple analysis we shall neglect this shrinkage. Charge pumps made of samples with large electric polarization in the direction perpendicular to the electrodes have larger efficiency. A perpendicular polarization can be achieved by applying a voltage between the electrodes. Indeed, a simple extension of the approach of reference reveals that for voltages higher than \( V_c = 2bP_s^0/(\varepsilon_0\varepsilon_1) \) the sample’s polarization is perpendicular to the electrodes. For \( b = 10 \text{ nm}, \varepsilon_1 = 10 \), and for a SmC* phase with \( P_s^0 = 550 \text{ nC/cm}^2 \) we get a small voltage \( V_c = 1.25 \text{ V} \). We see that the polarization will have the required direction provided that the voltage \( V_1 \) (Fig. 2) is greater than \( V_c \).

Typically one deals with SmC* hosts doped with dye molecules, whose number fraction is a few percent. The behavior of the average polarization after time \( t_{on} \) can be described theoretically. Here we shall simply suppose that the light is sufficiently intense so that there is a time \( t_{on} < t_{off} \) such that \( P_{in}(t_{on}) \) vanishes. In other words, we can regard \( t_{on} \) as the minimal time needed for a sufficient depletion of the trans dye population to eliminate the polarization. Taking \( P_{in}(t_{on}) = 0 \), formula \( 3 \) for the voltage \( V_{on} \) reduces to \( V_{on} = V_1 + LP_s^0/\varepsilon_0\varepsilon_1 \). For instance, for a SmC* material with \( P_s^0 = 550 \text{ nC/cm}^2 \) and \( \varepsilon = 4 \) in a cell of thickness \( L = 2 \mu \text{m} \) one obtains a \( V_{on} - V_1 \approx 310 \text{ V} \), which is much larger than \( V_1 \). Therefore, the optimal voltage \( V_2 \) is \( V_{2opt} \approx 155 \text{ V} \).
mol% of a racemic mixture of W470 azo dyes. An example a polar SmC* host W314 doped with a few dye molecules per unit volume that need to be captured more of the broad solar spectrum. A gradient of thermal recovery of spontaneous polarization, and the integral goes from the dark state temperature to the dark state polarization $P_s$ (9).

Let us briefly consider the case of a non-zero polarization profile through the sample. We adopt a simple model for this profile, namely, we assume that the polarization is eliminated in a layer of thickness $\Delta L$, while in the rest of the sample it is uniform and equal to the dark state polarization $P_s^0$. Then we can write $P_s^0 = \int_0^L P_s(x)dx/L = P_s^0(L - \Delta L)/L$. As $I_{s\text{on}}n_{\text{on}}A$ can be roughly estimated as $U_{\text{in}}\Delta L$, for the power efficiency we get $\eta = (P_s^0)^2\Delta L/(4\varepsilon_0\varepsilon U_{\text{in}}L)$. The efficiency is, therefore, reduced by a factor of $\Delta L/L$ with respect to (9).

Our pump could equally work on cycles of temperature change that change the spontaneous polarization. In this case the input energy is $U_{\text{in}} = \eta_{\text{tot}} \int C(T)dT$, where $C(T)$ is the specific heat per molecule at temperature $T$, and the integral goes from the dark state temperature of ferroelectric material to the temperature where the spontaneous polarization is eliminated (SmC*-SmA* phase transition temperature for liquid crystals). The heat that is unavoidably generated by optical absorption thus adds to the efficiency of our optical energy harvester.

In summary, we have proposed a light-powered charge pump for energy conversion, using a photoferroelectric working material. The efficiency is explicitly given, which makes clear directions for further increase.

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Supposing that $P_s(t_{\text{on}}) = 0$, the efficiency $\eta$ is provided that $t_{\text{on}}$ is shorter than the characteristic time of thermal recovery of spontaneous polarization, and the process of back photoconversion from the cis to the trans state of dye molecules can be neglected, the input energy can be expressed as $U_{\text{in}} = n_d\hbar\omega$. Here $n_d$ is the number of dye molecules per unit volume that need to be converted to cis to eliminate $P_s$, and $\omega$ is the energy each dye molecule absorbs from the light beam.

To get a numerical estimate of the efficiency we take as an example a polar SmC* host W314 doped with a few mol% of a racemic mixture of W470 azo dyes (12,13). These two compounds have a very similar structure, the N=N double bond of W470 being the only difference. The polarization of the W314 host at $T = 31$ °C is roughly 550 nC/cm² and is one of the highest outside bent-core molecules (14). The trans absorption maximum of W470 dyes is located at 365 nm, which corresponds to photons of 3.4 eV. We assume that the quantum efficiency for the trans to cis transition is equal to 1. The relative molecular mass of W314 is 603, and assuming a density of roughly $10^3$ kg/m³, we obtain a total molecular number density $n_{\text{tot}} = 10^{27}$ molecules/m³. If only, say, 2% of molecules need to be converted to cis to eliminate the polarization, we obtain $n_d = 2 \times 10^{25}$ molecules/m³. Taking the dielectric constant of W314 in the direction perpendicular to the director $n$ (see Fig. 1) as $\varepsilon = 4$, the efficiency (9) is $\eta \approx 2\%$. Multiple layers with different dyes which absorb photons of different energies would capture more of the broad solar spectrum. A gradient of dye species can be stabilized by bonding them into an elastomeric SmC* host – a loosely linked solid that is still able to change its degree of order. Such solids also reduce the risk of charge transport under fields ($V_2/L$ here) as in dielectric actuation using rubber. Lower energy photons would give correspondingly higher efficiencies $\eta \sim 2\%$.

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