

Static-EMF solid conductor P, polar liquid L, solid conductor N, capacitor

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Abstract

Energy conversion derived from the electric double layer at solid/liquid interfaces based on electrokinetic effects constitutes motional electromotive force. This study investigates static electromotive force that statically manifests and releases the electric field energy of the solid/liquid contact electric double layer. To this end, a special capacitor composed of solid conductor P/polar liquid L/solid conductor N (P/L/N capacitor) is constructed. The research reveals: (i) The contact electric double layer polarized by the internal potential difference of the solid conductor/polar liquid is equivalent to the electric double layer polarized by an external electric field in conventional capacitors. The formation process of the contact electric double layer represents the spontaneous charging process of the P/L/N capacitor, which statically manifests the electric field energy of the contact electric double layer. (ii) Because the polarized external potential difference of the solid conductor/polar liquid contact electric double layer is always smaller than its internal potential difference, the short-circuited P/L/N capacitor after discharge retains a persistent electromotive force, thereby statically releasing the electric field energy of the contact electric double layer. (iii) The contact electric double layer of the solid conductor/polar liquid is spontaneously generated through mutual contact, representing a self-organizing process that absorbs ambient thermal energy and converts it into the electric field energy of the contact electric double layer. The P/L/N capacitor achieves thermoelectric conversion by releasing the electric field energy of the contact electric double layer. This provides possibilities for developing self-generating capacitors, self-powered power supplies, and related devices.

Full Text

Static Electromotive Force in Solid-State Conductor P/Polar Liquid L/Solid-State Conductor N Capacitors

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Abstract

Energy conversion from the solid/liquid contact electric double layer based on electrokinetic effects generates dynamic electromotive force. This paper investigates static electromotive force that manifests and releases the electric field energy of the solid/liquid contact electric double layer through a novel capacitor structure: solid-state conductor P/polar liquid L/solid-state conductor N (P/L/N capacitor). Experimental findings reveal: (i) The contact electric double layer polarized by the internal potential difference of the solid conductor/polar liquid is equivalent to that polarized by an external electric field in conventional capacitors. The formation process of the contact electric double layer constitutes a spontaneous charging process of the P/L/N capacitor, which statically manifests the electric field energy of the contact electric double layer. (ii) Since the polarized external potential difference of the solid conductor/polar liquid contact electric double layer is always smaller than its internal potential difference, a short-circuited P/L/N capacitor maintains a continuous electromotive force after discharge, thereby statically releasing the electric field energy of the contact electric double layer. (iii) The solid conductor/polar liquid contact electric double layer arises spontaneously from mutual contact, representing a self-organizing process that absorbs ambient thermal energy and converts it into electric field energy. The P/L/N capacitor thus achieves thermoelectric conversion by releasing this stored electric field energy. These findings provide a foundation for developing self-generating capacitors and self-powered power sources.

Keywords: solid conductor/polar liquid; contact electric double layer; thermoelectric conversion; electromotive force

Electrokinetic effects, first discovered in 1807, encompass a series of phenomena at solid/liquid interfaces where fluid flow generates electricity or electric fields induce fluid motion. Classical electrokinetic phenomena include electrophoresis, electroosmosis, streaming potential, and sedimentation potential, all originating from the electric double layer at solid/liquid interfaces [1]. Recent years

have witnessed the development of high instantaneous power density generators based on droplets [2], hydrovoltaic materials and energy converters based on nanocarbon [3], and energy harvesting from water-graphene interactions [4]. Sustainable self-sufficient power sources for micro/nano-systems represent an emerging field in energy research [5], making these novel energy converters based on solid/liquid interface electrokinetic effects a hot research topic. This paper posits that the electrical energy in such converters derives from the electric field energy of the contact electric double layer at solid/liquid interfaces. Just as dynamic electrokinetic effects through contact and separation can convert this electric field energy into dynamic electromotive force, static methods can similarly manifest and release the electric field energy of the contact electric double layer to generate static electromotive force.

Conventional capacitors consist of two homogeneous solid conductors separated by a dielectric thin film, where an external electric field polarizes the dielectric to form an electric double layer, resulting in a charged capacitor [6]. When any two different phases contact, an internal potential difference (Galvani potential difference) arises between them, which cannot be measured directly. This internal potential difference polarizes a contact electric double layer possessing an external potential difference (Volta potential difference) that can be measured directly [7]. This paper argues that the contact electric double layer polarized by the internal potential difference of a solid conductor/polar liquid is equivalent to that polarized by an external electric field in conventional capacitors. To investigate this, we constructed a special solid-state conductor P/polar liquid L/solid-state conductor N capacitor (P/L/N capacitor), where no redox reactions occur between the solid conductors and polar liquid. Examples include platinum/water/graphite capacitors (Pt/H₂O/C capacitors), which exhibit two structural configurations: an open-circuit capacitor formed by P/L junction and L/N junction, and a short-circuited capacitor formed by P/L junction, L/N junction, and N/P junction.

1.1 Materials and Instruments

1. **Solid Conductors P and N:** Pt sheet ($99.99 \times 30 \times 0.3 \text{ mm}$), Au sheet ($99.99 \times 30 \times 0.3 \text{ mm}$, polycrystalline ($99.99 \times 30 \text{ mm}$), carbon rod ($99.99 \times 30 \text{ mm}$), conductive ceramic rod ($MoSi_2$) ($\Phi 8 \times 30 \text{ mm}$). Semiconductor wafers Si(11N, P-type, $4" \times 1 \text{ mm}$) and Si(11N, N-type, $4" \times 1 \text{ mm}$) were used for comparative experiments.
2. **Dielectrics:** Polar liquid L included formamide (H₃CON), water (H₂O), glycerol (C₃H₈O₃), and acetone (C₃H₆O). Non-polar liquid carbon tetrachloride (CCl₄) and polar nano-powder barium titanate (BaTiO₃) were used for comparative experiments. All chemicals were analytically pure.
3. **Container:** 100 mL glass beaker.
4. **Instruments:** Potentiometer (UJ33A, 0.05%), voltmeter (17BMAX-01), microcurrent meter (measurement range: 19.99×10^{-12} A– 19.99×10^{-3} A), YET-720L high-precision dual-channel platinum

resistance temperature recorder (resolution 0.001°C).

1.2 Experimental Setup

As shown in [Figure 1: see original paper], the experimental setup consists of a beaker (2) containing polar liquid L (5) with a polymethyl methacrylate lid (1) fitted with two small holes. Solid conductor P (3) and solid conductor N (4) are immersed in polar liquid L (5) and suspended through the holes in the lid using pure nickel wires, maintaining a 30 mm separation between the conductors. The entire apparatus is placed in a uniform temperature environment. For open-circuit P/L/N capacitors, the potential difference is denoted as U_c , with maximum value U_{mc} ; for short-circuited P/L/N capacitors, the voltage is U_o and current is I_o , with minimum values U_{mo} and I_{mo} , respectively.

1.3 Experimental Results

1. Relationship between P/L/N capacitor electromotive force and energy source. Using Pt/H₂O/Au capacitors as an example, Pt and Au are inert solid conductors that do not undergo redox reactions with H₂O. High-purity Pt and Au sheets were first immersed in HF solution to remove trace surface impurities before assembling the Pt/H₂O/Au capacitor, which was then placed in a sealed, temperature-uniform metal container to eliminate interference from electrokinetic effects, thermoelectric effects, electromagnetic induction, photoelectric effects, concentration cells, and chemical primary cells. The experimental data shown in [Figure 2: see original paper], [Figure 3: see original paper], and Table 1 (first group) provide evidence that the electric field energy of P/L/N capacitors can only originate from ambient thermal energy.

2. Relationship between P/L/N capacitor electromotive force and time. As shown in [Figure 2: see original paper], at a uniform ambient temperature of 25°C, the open-circuit Pt/H₂O/Au capacitor exhibits spontaneous charging, with the potential difference U_c between its electrodes gradually increasing to a stable, sustained maximum value U_{mc} of 132 mV (see Table 1, first group). When this Pt/H₂O/Au capacitor is short-circuited, it exhibits a discharge state, with the voltage U_o and current I_o gradually decreasing to stable, sustained minimum values U_{mo} of 18 mV and I_{mo} of 0.08 A (see Table 1, first group). Switching the short-circuited Pt/H₂O/Au capacitor back to open-circuit configuration restores the spontaneous charging state, demonstrating a repeatable cycle. This provides experimental evidence for static electromotive force generation in P/L/N capacitors.

3. Relationship between P/L/N capacitor electromotive force and temperature. As shown in [Figure 3: see original paper], under uniform ambient temperature conditions with a heating rate of 1 K/h, both the potential difference U_c of open-circuit Pt/H₂O/Au capacitors and the voltage U_o of short-circuited Pt/H₂O/Au capacitors exhibit a linear positive correlation with temperature. This provides experimental basis for analyzing temperature effects on

P/L/N capacitors.

4. Relationship between P/L/N capacitor electromotive force and solid conductor materials. With polar liquid L fixed as H_2O , Table 1 (first two groups) shows the effects of different solid conductor materials on P/L/N capacitor performance, while Table 1 (middle two groups) demonstrates the influence of different crystal forms of the same material. The Si(P)/ H_2O /Si(N) capacitor composed of two solid semiconductors exhibits significant photoelectric effects, but measurable electromotive force and current can still be obtained under dark conditions (Table 1, last group). This provides experimental evidence for analyzing the roles of solid conductors P and N in P/L/N capacitors.

Table 1 : Electromotive force of P/ H_2O /N capacitors at uniform temperature 25°C

Capacitor Type	U _{mc} (mV)	U _{mo} (mV)	Imo (A)
Pt/ H_2O /Au	132	18	0.08
Pt/ H_2O /C			
C*/ H_2O /MoSi ₂			
C**/ H_2O /MoSi ₂			
Si(P)/ H_2O /Si(N)			

5. Relationship between P/L/N capacitor electromotive force and dielectric properties. With solid conductor P fixed as graphite (C) and solid conductor N as metal Ni, comparative measurements were performed using different dielectrics. Table 2 (first four groups) shows that the internal potential difference at solid conductor/polar liquid interfaces enables polar molecules in the liquid to overcome intermolecular forces, rotate, and align their dipole moments, generating electromotive force correlated with dielectric constant. Table 2 (middle group) demonstrates that with non-polar liquid CCl_4 as dielectric, the internal potential difference is insufficient to polarize non-polar molecules, resulting in no electromotive force. Table 2 (last group) shows that with polar nano-powder $BaTiO_3$ as dielectric, the internal potential difference cannot polarize $BaTiO_3$ grains or molecules, also yielding no electromotive force. This provides experimental basis for analyzing the role of polar liquid L in P/L/N capacitors.

Table 2 : Electromotive force of C/L/Ni capacitors at uniform temperature 25°C

Capacitor Type	U _{mc} (mV)	U _{mo} (mV)
C/ H_3CON /Ni		
C/ H_2O /Ni		
C/ $C_3H_8O_3$ /Ni		
C/ C_3H_6O /Ni		

Capacitor Type	U _{mc} (mV)	U _{mo} (mV)
C/CCl ₄ /Ni	266	104~105
C/BaTiO ₃ /Ni		

2 Analysis and Discussion

2.1 Mechanism of Static Electromotive Force in P/L/N Capacitors

To understand how P/L/N capacitors statically manifest and release the electric field energy of solid conductor/polar liquid contact electric double layers, we must examine their unique structure and properties. Any interface between two different phases exhibits an internal potential difference, creating a built-in electric field and contact electric double layer [8]. However, solid conductor/polar liquid interfaces possess distinct structural and property characteristics compared to solid/solid and solid/liquid interfaces.

As illustrated in Figure 2: see original paper and (b), at solid conductor P/solid conductor N interfaces, charge diffusion and exchange across the P/N junction under internal potential difference U_{PN} creates a contact electric double layer spanning both phases. The internal potential difference U_{PN} and the induced external potential difference U'_{NP} are equal in magnitude but opposite in direction, reaching dynamic equilibrium. In semiconductor P/N junctions, this contact electric double layer is characterized by barrier capacitance and diffusion capacitance [9].

German physicist Helmholtz proposed the solid/liquid interface electric double layer theory as early as 1853, recognizing the double layer as the most universal and important phenomenon at solid/liquid interfaces, typically characterized by differential capacitance. Research on solid/liquid interface electric double layer structure and properties continues to evolve [10]. Building upon this foundation, we introduce dielectric theory in electrostatic fields [11] to investigate the special structure and properties of solid conductor/polar liquid contact electric double layers.

As shown in Figure 2: see original paper and (b): (i) The P/L and L/N junctions in P/L/N capacitors are solid conductor/polar liquid interfaces where no redox reactions or charge diffusion exchange occur, so the internal potentials of solid conductors P and N remain unchanged, with the contact electric double layer appearing only within polar liquid L without spanning both phases. (ii) Polar molecules in liquid L overcome intermolecular forces under the internal potential differences at P/L and L/N junctions, causing their electric dipole moments to undergo ordered reorientation and align at the interfaces, generating polarization surface charges that cause solid conductors P and N to exhibit the potentials of their respective contact electric double layers. The two differential capacitances at P/L and L/N junctions thus function as capacitive elements. (iii) The different internal potentials of solid conductors P and N produce dif-

ferent external potentials, creating an external potential difference between the conductors. The P/L and L/N junctions, as two capacitive elements, combine to form a P/L/N capacitor, making the open-circuit P/L/N capacitor equivalent to a conventional charged capacitor that spontaneously generates charge, thereby statically presenting the electric field energy of the contact electric double layer. (iv) Due to molecular thermal motion, the dipole moments of polar molecules cannot align perfectly with the internal potential difference direction of the solid conductor/polar liquid interface, so the external potential difference of the polarized P/L and L/N junction contact electric double layers is always smaller than their internal potential difference. Since the P/N junction's external potential difference equals its internal potential difference, the P/L-L/N-P/N junction combination forms a short-circuited P/L/N capacitor that maintains a continuous electromotive force after discharge.

As depicted in Figure 2: see original paper and (b), polar liquid L under internal potential differences U_{PL} and U_{LN} at P/L and L/N junctions becomes polarized to form contact electric double layers, creating two charged capacitive elements CPL and CLN with external potential differences U'_{LP} and U'_{NL} . As shown in Figure 2: see original paper, these two capacitive elements combine into a P/L/N capacitor CPN, with the two external potential differences U'_{LP} and U'_{NL} combining into the capacitor potential difference U_c . Thus, the open-circuit P/L/N capacitor is an inherently charged capacitor produced by P/L and L/N junctions. If solid conductors P and N develop the same type of polarization surface charge q , the two capacitive elements are connected in parallel; otherwise, they are in series. The total capacitance is C , and the contact electric double layer electric field energy is We .

$$(1)$$

$$(2)$$

qU

$$(3)$$

Furthermore, the P/N junction's internal potential difference depends only on the solid conductor material properties. The external potential difference formed by charge diffusion is:

$$0 \quad 0$$

$$(4)$$

where k is the Boltzmann constant, e is the electron charge, σ_N and σ_P are the free electron densities of solid conductors N and P, and T is the thermodynamic temperature [12].

The P/L and L/N junctions involve solid conductor/polar liquid contacts where the internal potential difference depends on both material properties and the solid conductor's surface state, structure, and internal forces. Considering the complexity of solid conductor surfaces, we introduce a function α to modify the

surface potential. If the dielectric constant of polar liquid L at temperature T is ϵ , the external potential differences generated under internal potential difference polarization at P/L and L/N junctions are:

$$\phi_{P/L} = \frac{q}{4\pi\epsilon_0\epsilon} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (5)$$

$$\phi_{L/N} = \frac{q}{4\pi\epsilon_0\epsilon} \left(\frac{1}{r_3} - \frac{1}{r_4} \right) \quad (6)$$

As shown in Figure 2: see original paper, the open-circuit P/L/N capacitor potential difference $U_c(T)$ is the combination of the P/L and L/N junction external potential differences:

$$U_c(T) = \phi_{P/L} + \phi_{L/N} \quad (7)$$

As shown in Figure 2: see original paper, the short-circuit P/L/N capacitor electromotive force $U_e(T)$ is the combination of external potential differences from P/L, L/N, and P/N junctions:

$$U_e(T) = \phi_{P/L} + \phi_{L/N} + \phi_{P/N} \quad (8)$$

For a short-circuit P/L/N capacitor with internal resistance r and external resistance R , the circuit current I_o and voltage U_o at temperature T are:

$$I_o = \frac{U_e(T)}{R + r} \quad (9)$$

$$U_o = I_o R \quad (10)$$

These calculations demonstrate that at uniform temperature, without charge diffusion exchange between solid conductor and polar liquid, the internal potentials of solid conductors remain constant. The different free electron concentrations σ_N and σ_P in solid conductors P and N polarize contact electric double layers with unequal external potential differences in polar liquid L. Consequently, the non-conservative force underlying P/L/N capacitor electromotive force is essentially the free electron concentration difference between solid conductors P and N caused by electron thermal motion.

Although polar liquid L is a dielectric, it contains trace mobile free charges (e.g., H^+ and OH^- in H_2O). While no charge exchange or diffusion occurs at solid conductor/polar liquid interfaces, electron transfer can still be realized. Detailed explanations are provided in studies on electron and ion transfer induced by contact electrification at liquid-solid interfaces [13], quantitative research on electron transfer in solid-liquid contact electrification [14], and two-step mechanism models of interfacial electron transfer and electric double layer structure in liquid-solid contact [15]. Therefore, short-circuited P/L/N capacitors after discharge can sustain voltage and current to continuously release the electric field energy of the contact electric double layer, achieving static electromotive force generation.

2.2 Mechanism of Thermoelectric Conversion in P/L/N Capacitors

Since P/L/N capacitors statically manifest and release the electric field energy of solid conductor/polar liquid contact electric double layers, we must investigate the energy source of this electric field. Statistical mechanical treatments of entropy formation in the inner layer of electrode/solution interfaces [16] can be analogously applied to solid conductor/polar liquid interfaces. Because no charge exchange occurs between solid conductor and polar liquid, the free electron densities in solid conductors P and N remain unequal. Moreover, since P/L and L/N junctions are interphase transition regions with fundamentally different bulk properties, the P/L/N capacitor constitutes a non-equilibrium thermodynamic system.

The actual process occurs in an open system under atmospheric conditions. As an enormous heat source, the atmosphere undergoes infinitesimal temperature and pressure changes when exchanging finite heat with individual polar liquid molecules in the capacitor. Thus, the temperature T of a P/L/N capacitor can be considered invariant before and after heat absorption or release during polarization of a single polar liquid molecule. If the unit polarization surface charge is dq with minimum charge e , the electric field energy of a unit polarization surface charge is dWe :

$$\text{-----} \quad (11)$$

The ordered reorientation of one degree of freedom of a polar liquid molecule's electric dipole moment reduces its internal energy by dE :

$$\text{-----} \quad (12)$$

According to the first law of thermodynamics:

$$dQ = dW + dE \quad (13)$$

The entropy change dS of the capacitor is therefore:

$$\text{-----} \quad (14)$$

Since the dielectric constant of polar liquid is always greater than 1, as long as $\sigma_N \neq \sigma_P$:

$$\text{-----} \quad (15)$$

These calculations indicate that because of polar liquid L always exceeds 1, whenever the free electron concentrations σ_N and σ_P of solid conductors P and N differ sufficiently, the P/L/N capacitor can maintain an ordered state. This demonstrates that the P/L/N capacitor is a non-equilibrium dissipative structure where low-grade thermal energy can self-organize into high-grade electric field energy. The establishment of this ordered structure develops spontaneously within this open system, constituting a self-organizing phenomenon [17].

Polar molecules in liquid L undergo ordered reorientation under the internal potential differences at P/L and L/N junctions, overcoming intermolecular forces and reducing internal energy while polarizing the contact electric double layers and increasing electric field energy. To maintain uniform temperature, the capacitor must absorb ambient thermal energy to compensate for the reduced internal energy. Through this process, the solid conductor/polar liquid interface converts ambient thermal energy into electric field energy of the contact electric double layer. Thus, the formation of solid conductor/polar liquid contact electric double layers is a self-organizing process that converts thermal energy to electric field energy, enabling P/L/N capacitors to achieve thermoelectric conversion by releasing this stored energy.

1. Because no charge exchange occurs between solid conductor and polar liquid, the contact electric double layer appears only within the polar liquid, causing the solid conductors to exhibit the external potential difference of the contact electric double layer and form charged capacitive elements. Two such charged capacitive elements combine to create an open-circuit P/L/N charged capacitor, providing a method for spontaneous electromotive force generation.
2. The absence of charge exchange maintains constant potentials in both solid conductors, making the non-conservative force of P/L/N capacitor electromotive force the free electron concentration difference between solid conductors P and N caused by electron thermal motion. Since the internal potential difference of solid conductor/polar liquid exceeds the polarized external potential difference, short-circuited P/L/N capacitors after discharge can sustain continuous voltage and current to release the electric field energy of the contact electric double layer, providing a method for static electromotive force generation.
3. As a non-equilibrium dissipative structure, the solid conductor/polar liquid interface can absorb ambient thermal energy and self-organize it into electric field energy of the contact electric double layer, allowing P/L/N capacitors to statically manifest and release this energy and thereby providing a novel method for thermoelectric conversion.

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