# Statistical Electromotive Force of Solid-State Conductor P / Polar Liquid L / Solid-State Conductor N Capacitor

**Authors:** Zhengliang Wang, Shanfei Chen, Gelin Wang, Zhengliang Wang, Gelin Wang

**Date:** 2023-12-09T00:00:00+00:00

## Abstract

Based on the principle that the energy conversion of the dynamic electric effect from the solid/liquid contact double electric layer constitutes the dynamic electromotive potential, this paper investigates the static manifestation and the release of the electric field energy of the solid/liquid contact double electric layer, and consequently constructs a special capacitor (P/L/N capacitor) comprising solid conductor P / polar liquid L / solid conductor N. The experimental observations are as follows: (i) The contact double electric layer formed by the polarization of the internal potential difference of the solid conductor/polar liquid is equivalent to the external electric field polarization of an ordinary capacitor. The formation process of the contact double electric layer is the spontaneous charging process of the P/L/N capacitor, and the P/L/N capacitor still exhibits the electric field energy of the contact double electric layer. (ii) Because the polarized external potential difference of the solid conductor/polar liquid contact double electric layer is always less than the internal potential difference, the short-circuited P/L/N capacitor still possesses a continuous electromotive force after discharge, thereby statically releasing the electric field energy of the contact double electric layer. (iii) The contact double electric layer of solid conductor/polar liquid is spontaneously generated upon mutual contact, and it also represents a self-organizing process that absorbs environmental heat energy into the electric field energy of the contact double electric layer. P/L/N capacitors achieve thermoelectric conversion by releasing the electric field energy of the contact double electric layer. The aforementioned phenomenon provides the possibility for developing self-generated capacitors and self-supplied power supplies.

## Full Text

## Preamble

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

Zhengliang Wang[1],, *Shanfei Chen*[1], *Gelin Wang*[2],[3],
[1] Zhejiang Wanli University, Ningbo, China, 315100
[2] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China, 315100
[3] University of Nottingham Ningbo China, Ningbo, China, 315100
*E-mail: wzl111@zwu.edu.cn; wanggelin@nimte.ac.cn*

**Abstract:** While the dynamic electric effect at solid/liquid contact interfaces converts energy through the electric double layer to produce dynamic electromotive potential, this work investigates the static manifestation and release of electric field energy from the solid/liquid contact electric double layer. We constructed a special capacitor—the P/L/N capacitor—comprising a solid conductor P, polar liquid L, and solid conductor N. Experimental observations reveal three key phenomena: (i) The contact electric double layer formed by internal potential difference polarization at the solid conductor/polar liquid interface is equivalent to the external electric field polarization in ordinary capacitors. The formation process of this contact double layer constitutes spontaneous charging of the P/L/N capacitor, which retains the electric field energy of the contact double layer. (ii) Because the polarized external potential difference at the solid conductor/polar liquid contact interface is always smaller than the internal potential difference, even short-circuited P/L/N capacitors exhibit continuous electromotive force after discharge, thereby statically releasing the electric field energy of the contact double layer. (iii) The solid conductor/polar liquid contact double layer forms spontaneously upon contact, representing a self-organizing process that absorbs ambient thermal energy and converts it into electric field energy. P/L/N capacitors thus achieve thermoelectric conversion by releasing this stored electric field energy. These phenomena provide a foundation for developing self-charging capacitors and self-powered energy supplies.

**Keywords:** Solid conductor/polar liquid; contact electric double layer; thermoelectric conversion; electromotive force.

## Introduction

The kinetic effect, first discovered in 1807, encompasses a series of flow-generated or electrically induced fluid motion phenomena at solid/liquid interfaces, including electrophoresis, electroosmosis, flow potential, and sedimentation potential. The fundamental mechanism underlying these classical kinetic phenomena originates from the action of the electric double layer at the solid/liquid interface [1]. Recent advances have demonstrated high instantaneous power density generators based on liquid droplets [2], nanocarbon-based hydrovoltaic materials with energy conversion capabilities [3], and energy harvesting from water-graphene interactions [4]. Sustainable self-powered systems for micro- and nanoscale applications have emerged as a significant field in energy research [5], making such solid/liquid interface energy converters based on kinetic effects a hot topic for investigation and development. This paper argues that the electrical energy in these converters derives from the electric field energy of the contact electric double layer at the solid/liquid interface. This energy can be harnessed either through dynamic electromotive force (EMF) generated by contact-separation processes or through static electromotive force (SEF) achieved by statically revealing and releasing the electric field energy of the contact double layer.

An ordinary capacitor consists of two homogeneous solid conductors with a dielectric film between them. When an external electric field is applied, the dielectric becomes polarized, forming an electric double layer and charging the capacitor [6]. Any contact between two different phases creates an internal potential difference between them, known as the Galvani potential difference, which cannot be measured directly. However, the contact electric double layer generated by this internal potential difference exhibits an external potential difference, known as the Volta potential difference, which is directly measurable [7]. Therefore, we propose that the potential difference polarizing the contact double layer within a solid conductor/polar liquid system is equivalent to that polarizing the double layer in an ordinary capacitor under an applied electric field.

To investigate this phenomenon, we constructed a special P/L/N capacitor comprising solid conductor P, polar liquid L, and solid conductor N, where no redox reactions occur between the solid conductors and the polar liquid. As demonstrated by the platinum/water/graphite capacitor (Pt|$H_2O$|C capacitor), this device can be configured in two structural forms: an open-circuit capacitor formed by P/L and L/N junctions, or a short-circuit capacitor formed by P/L, L/N, and N/P junctions.

### 2.1 Reagents and Instruments

1) **Inert Conductors P and N**: Electronic conductors including platinum (Pt, $ 99.99×30×$0.3 mm), gold (Au, $ 99.99×30×0.3mm, polycrystalline), graphitesheetC( 99.9×30×3m ( 99.99×30mm), carbonrodC**( 99.99×30mm), andconductiveceramicrodMoSi_{2}$ (Φ8$×30mm).SemiconductorwafersSi(11N, P−type, 4"×1mm)andSi(11N, N−type, 4"×$1 mm) were used for comparative experiments.

2) **Dielectric Materials**: Polar liquid L included formamide ($H_3CON$), water ($H_2O$), glycerol ($C_3H_8O_3$), and acetone ($C_3H_6O$). Non-polar carbon tetrachloride ($CCl_4$) and polar nano-powder barium titanate ($BaTiO_3$) were used for comparison. All chemicals were analytically pure.

3) **Containers**: 100 mL glass beakers.

4) **Instrumentation**: Potential difference meter (UJ33A, 0.05% ac-

curacy), voltmeter (17BMAX-01), microammeter (measurement range: 19.99$\times10^{-12}$ A to 19.99$\times10^{-3}$ A), and YET-720L high-precision dual-channel platinum resistance temperature recorder (resolution 0.001°C).

### 2.2 Experimental Device

As shown in [Figure 1: see original paper], the experimental setup consists of a Pt/$H_2O$/Au capacitor with a schematic diagram of the P/L/N capacitor configuration. A beaker (2) is filled with polar liquid L (5) and sealed with a Plexiglas lid (1) containing two small holes. Solid conductor P (3) and solid conductor N (4) are immersed in the polar liquid L (5) and suspended through the holes using pure nickel conductive 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, we measured the potential difference Uc and its maximum stable value Umc. For short-circuit configurations, we measured the voltage Uo and current Io, as well as their minimum stable values Umo and Imo.

**Figure 1**: Experimental photograph of Pt/$H_2O$/Au capacitors and schematic diagram of P/L/N capacitors.

### 2.3 Experimental Results

1) **Electric Potential of P/L/N Capacitor versus Energy Source**: Using the Pt/$H_2O$/Au capacitor as an example, Pt and Au are typical inert solid conductors that do not undergo redox reactions with $H_2O$. High-purity Pt and Au electrodes were first immersed in HF solution to remove trace surface impurities, then assembled into a Pt/$H_2O$/Au capacitor and placed statically in a sealed metal container at uniform temperature. This configuration excludes disturbances from kinetic electric effects, thermoelectric effects, electromagnetic induction, photoelectric effects, concentration cells, and chemical batteries. Experimental data were collected as shown in [Figure 2: see original paper], [Figure 3: see original paper], and Table I (first group), providing evidence that the electric field energy in P/L/N capacitors can only originate from ambient thermal energy.

2) **Electric Potential versus Time**: As shown in [Figure 2: see original paper], at a uniform ambient temperature of 25°C, the open-circuit Pt/$H_2O$/Au capacitor exhibits spontaneous charging, with the interelectrode potential difference Uc gradually increasing over time until reaching a stable maximum value Umc of 132 mV (see Table I, first group). When short-circuited, the capacitor discharges, with the voltage Uo and current Io between the electrodes gradually decreasing to stable minimum values of Umo = 18 mV and Imo = 0.08  A (see Table I, previous group). Switching the short-circuited Pt/$H_2O$/Au capacitor back to open-circuit configuration results in spontaneous charging again, demonstrating the

static generation of electromotive force in P/L/N capacitors.

3) **Electric Potential versus Temperature**: As shown in [Figure 3: see original paper], both the open-circuit potential difference Uc and short-circuit voltage Uo of the Pt/$H_2O$/Au capacitor exhibit a linear positive correlation with temperature under uniformly increasing ambient temperature (1 K/h). This provides an experimental basis for analyzing temperature effects on P/L/N capacitors.

4) **Electric Potential versus Solid Conductor Materials**: With polar liquid L fixed as $H_2O$, Table I (first two groups) shows the influence of different solid conductor materials on capacitor performance. Table I (middle two groups) demonstrates the effect of solid conductors with identical composition but different crystal structures. The Si(P)/$H_2O$/Si(N) capacitor, combining two solid-state semiconductors, exhibits a measurable photoelectric effect, yet electric potential and current can still be measured in the absence of illumination (Table I, latter group), providing insight into the roles of solid conductors P and N.

5) **Electric Potential versus Dielectric Material**: Using graphite C for both solid conductors P and metal Ni for solid conductors N, we conducted comparative measurements with different dielectrics. Table II (first four groups) demonstrates that the internal potential difference at solid conductor/polar liquid interfaces can overcome intermolecular forces, causing polar molecules to rotate and align their dipole moments, thereby generating electric potentials that correlate with dielectric constants. In contrast, Table II (middle group) shows that with non-polar liquid $CCl_4$ as the dielectric, the internal potential difference is insufficient to polarize non-polar molecules, resulting in no measurable electric potential. Similarly, Table II (latter group) shows that with polar nano-powder $BaTiO_3$ as the dielectric, the internal potential difference cannot polarize the grains or molecules, and no potential is observed. These results clarify the essential role of polar liquid L in P/L/N capacitors.

**Table 1** : Electromotive force of P/$H_2O$/N capacitors at uniform temperature (25°C).

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

### 3.1 Mechanism of Static Electric Potential Generation in P/L/N Capacitors

Understanding how P/L/N capacitors statically manifest and release the electric field energy of solid conductor/polar liquid contact double layers requires examination of the special structure and properties of these interfaces. Any contact interface between two different physical phases exhibits an internal potential difference that creates an internal electric field and generates a contact electric double layer [8]. However, the solid conductor/polar liquid contact double layer possesses unique structural and behavioral characteristics compared to solid/solid and solid/liquid interfaces.

As illustrated in Figure 4: see original paper and (b), the contact interface between solid-state conductors P and N involves charge exchange through diffusion under the internal potential difference of the P/N junction, forming a contact double layer that spans both phases. The internal potential difference UPN is equal in magnitude and opposite in direction to the external potential difference U'NP, establishing dynamic equilibrium characterized by barrier capacitance and diffusion capacitance in semiconductor P/N junctions [9].

German physicist Hermann von Helmholtz first presented the electric double layer theory for solid/liquid interfaces in 1853, recognizing it as the most common and important interfacial phenomenon. Solid/liquid contact double layers are generally characterized by differential capacitance, and their structure and properties have been continuously studied and refined [10]. This paper introduces electrostatic field dielectric theory [11] to investigate the special structure and properties of solid conductor/polar liquid contact double layers.

As shown in Figure 4: see original paper and (b), three key features distinguish the P/L/N capacitor: (i) The P/L and L/N junctions are solid conductor/polar liquid interfaces where neither redox reactions nor charge diffusion exchange occur between phases, so the internal potentials of solid conductors P and N remain unchanged, and the contact double layer appears only within polar liquid L without spanning both phases. (ii) Polar molecules in liquid L overcome intermolecular forces under the potential differences at P/L and L/N junctions, causing orderly reorientation of their electric dipole moments at these interfaces. This creates polarized surface charges that induce contact double layer potentials on solid conductors P and N, with the two differential capacitances of the P/L and L/N junctions acting as two capacitive elements. (iii) The unequal internal potentials of solid conductors P and N produce different external potentials, and the external potential difference between them indicates that the P/L and L/N junctions combine to form a P/L/N capacitor. Consequently, an open-circuit P/L/N capacitor is equivalent to an ordinary charged capacitor that spontaneously generates charge, statically manifesting the electric field energy of the contact double layer. (iv) Because thermal motion prevents perfect alignment of polar molecule dipole moments with the internal potential difference, the external potential difference of the polarized P/L and L/N junctions is always smaller than the internal potential difference. In contrast, the P/N junction's external potential difference equals its internal potential difference. Therefore, the P/L junction-L/N junction-P/N junction configuration creates a short-circuited P/L/N capacitor that maintains continuous electric potential after discharge.

As shown in Figure 4: see original paper and (b), the internal potential differences UPL and ULN at the P/L and L/N junctions polarize the contact double layers, creating two charged capacitive elements CPL and CLN with external potential differences U'LP and U'NL. As illustrated in Figure 4: see original paper, these two elements combine to form the P/L/N capacitor CPN, with the external potential differences U'LP and U'NL combining to produce the capacitor potential difference Uc.

Therefore, an open-circuit P/L/N capacitor is an inherently charged device formed by P/L and L/N junctions. If the surfaces of solid conductors P and N are polarized with the same surface charge q, the two capacitive elements are connected in parallel; otherwise, they are in series. The total capacitance of the open-circuit P/L/N capacitor is C, and the electric field energy of the contact double layer is We:

———————————— (1)

———————————— (2)

qU ———————————— (3)

Because the internal potential difference of the P/N junction depends on the properties of the solid conductor materials, the external potential difference formed by mutual charge diffusion is:

() () ———————————— (4)

where is Boltzmann's constant, e is the electron charge, $\sigma$N and $\sigma$P are the free electron densities of solid conductors N and P, respectively, and T is the thermodynamic temperature [12].

For the P/L and L/N junctions, which involve solid conductor/polar liquid contacts, the internal potential difference depends on material properties, surface state, structure, and endogenous forces. Given the complexity of solid conductor surfaces, we introduce a function $\alpha$ to describe surface potential variations. If the dielectric constant of polar liquid L at temperature T is , the external potential differences generated under internal potential difference polarization at the P/L and L/N junctions are respectively:

———————————— (5)

———————————— (6)

As shown in Figure 4: see original paper, the potential difference Uc(T) of the open-circuit P/L/N capacitor is the combination of the external potential differences from the P/L and L/N junctions:

U T U () () () (() (———————————— (7)

As shown in Figure 4: see original paper, the potential Ue(T) of the short-circuited P/L/N capacitor combines the potential differences from the P/L junction, L/N junction, and external P/N junction:

() () () ———————————— (8)

For a short-circuited P/L/N capacitor with internal resistance r and external resistance R, the loop current Io and loop voltage Uo at temperature T are:

(9)

(10)

These calculations demonstrate that at uniform temperature, without charge diffusion exchange at the solid conductor/polar liquid interface, the potentials in the solid conductors remain constant. The non-conservative force generating the P/L/N capacitor's electric potential is inherently caused by the difference in free electron concentrations between solid conductors P and N, arising from thermal motion of electrons.

Although polar liquid L is a dielectric, it contains trace mobile charges such as $H^+$ and $OH^-$ ions in water. While no charge exchange or diffusion occurs at the solid conductor/polar liquid interface, electron transfer can still be realized. Recent studies have detailed contact charging-induced electron and ion transfer at liquid/solid interfaces [13], quantitative analysis of electron transfer initiation in solid-liquid contact [14], and two-step mechanistic modeling of interfacial electron transfer processes involving electric double layer structure [15]. Consequently, short-circuited P/L/N capacitors can maintain voltage and current after discharge, continuously releasing the electric field energy of the contact double layer and realizing static electric potential generation.

### 3.2 Thermoelectric Conversion Mechanism in P/L/N Capacitors

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

The actual operation of P/L/N capacitors occurs in an open atmospheric environment. The atmosphere serves as a vast heat source; when a finite amount of heat is exchanged with the minimal unit of a polar liquid molecule in the capacitor, the resulting temperature and pressure changes are infinitesimal. Therefore, the temperature T is considered invariant during polarization of a polar liquid molecule in the P/L/N capacitor. If the unit polarized surface charge is dq with minimum charge e, the electric field energy dWe of this unit surface charge is:

(11)

One degree of freedom of the polar liquid molecule's electric dipole moment becomes static, reducing the internal energy by dE:

(12)

According to the first law of thermodynamics:

dQ dW dE ———————— (13)

Transformation yields the entropy change dS of the capacitor:

———————————————— (14)

In the above equation, the dielectric constant of the polar liquid is always greater than 1, and provided $\sigma N \neq \sigma P$:

———————————————————————————— (15)

These calculations demonstrate that the dielectric constant of polar liquid L is always greater than 1. Meanwhile, as long as the difference between free electron concentrations $\sigma$N and $\sigma$P of solid conductors P and N is sufficiently large, the P/L/N capacitor can maintain an ordered state. This indicates that the P/L/N capacitor is a dissipative structure in non-equilibrium, where low-grade thermal energy can self-organize into high-grade electric field energy. The establishment of this ordered structure represents a self-organizing phenomenon in this open system [17].

Under the internal potential difference of P/L and L/N junctions, polar molecules in liquid L overcome intermolecular forces and undergo orderly reorientation, reducing internal energy and polarizing the contact double layers at these junctions. This increases the 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 double layer. Therefore, formation of the solid conductor/polar liquid contact double layer 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.

## Conclusion

1) Because no charge exchange occurs between solid conductor and polar liquid, the contact double layer forms only within the polar liquid, causing the solid conductors to exhibit external potential differences that create charged capacitive elements. Two such charged elements combine to form an open-circuit P/L/N charged capacitor, providing a method for spontaneous electric potential generation.

2) The absence of charge exchange maintains constant potentials in the two solid conductors, making the non-conservative force for the P/L/N capacitor's electric potential the difference in free electron concentrations between solid conductors P and N, caused by thermal motion of electrons. Since the internal potential difference at the solid conductor/polar liquid interface exceeds the polarized external potential difference, short-circuited P/L/N capacitors maintain continuous voltage and current after

discharge, releasing the electric field energy of the contact double layer. This provides a method for generating static electric potential.

3) As a dissipative structure in non-equilibrium, the solid conductor/polar liquid interface can absorb ambient thermal energy and self-organize it into electric field energy of the contact double layer. P/L/N capacitors thus generate static electric potential and release the electric field energy of the solid conductor/polar liquid contact double layer, offering a novel approach to thermoelectric conversion.

**Acknowledgement:** This research was funded by the Ningbo Public Welfare Science and Technology Program under Grant 2022S093.

## References

[1] Guo Wanlin, Fei Wenwen. Advances in the study of kinetic electric effects at solid-liquid interfaces. Vibration, Testing and Diagnostics [J], 2015, 35:603-615.
[2] Xu W, Zheng H, Liu Y, et al. A droplet-based electricity generator with high instantaneous power density. Nature 2020;578:392-6.
[3] Tan J, Tang Q W, He B L. Water voltaic materials and energy conversion device based on carbon nanomaterials (in Chinese). Chin Sci Bull, 2018, 63:2818-2832.
[4] Ji B X, Chen N, Zhang G F, et al. Power from water and graphene (in Chinese). Chin Sci Bull, 2018, 63:
[5] Wang Z L. Sustainable self-sufficient power source for micro/nano-systems: a new field in energy research (in Chinese). Chinese Sci Bull (Chinese Ver), 2010, 55: 2472-2475.
[6] Ma Wenwei et al. Tutorial of Physics. Beijing: Higher Education Press, 2002.
[7] Di Li. Principles of Electrochemistry [M]. Beijing: Beijing University of Aeronautics and Astronautics Press.
[8] Xiao Xianfan, Li Wenbin. Physical Chemistry [M]. Tianjin: Tianjin University Press, 2007.
[9] Cao Chunan. Principles of Corrosion Electrochemistry [M]. Beijing: Chemical Industry Press, 1985.
[10] Wang Guodong. University Physics [M]. Beijing: Higher Education Press, 2010.
[11] J.S. Lu, Z.L. Wang. Basic Physics Tutorial [M]. Harbin: Harbin Engineering University Press, 2006.
[12] Jiang Zhongliang, Chen Xiuyun. Measurement and Control of Temperature [M]. Beijing: Tsinghua University Press, 2005.
[13] Zuqing Yuan, Caofeng Pan. Quantifying electron-transfer in liquid-solid contact electrification. Science Bulletin 65 (2020) 868-869.
[14] Nie J, Ren Z, Xu L, et al. Probing contact-electrification-induced electron and ion transfers at a liquid-solid interface. Adv Mater 2020;32. 1905696.
[15] Chen XY, Liu Z Q, Wang Z L. The process of interfacial electron transfer in liquid-solid contact and the two-step mechanism model of EDL structure (in

Chinese). Sci Sin Tech, 2023, 53: 844-859.
[16] Su, W. Calc, Ye, H. Statistical mechanical treatment of entropy of formation of inner layers at electrode/solution interface. Journal of Physical Chemistry [J], 1993, 9: 351-355.
[17] Rusheng Li. Non-equilibrium Thermodynamics and Dissipative Structures [M]. Beijing: Tsinghua University Press, 1986.

*Note: Figure translations are in progress. See original paper for figures.*