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Contact Electrification at the Liquid–Solid Interface

Shiquan Lin,[§] Xiangyu Chen,[§] and Zhong Lin Wang*

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ABSTRACT: Interfaces between a liquid and a solid (L-S) are the most important surface science in chemistry, catalysis, energy, and even biology. Formation of an electric double layer (EDL) at the L-S interface has been attributed due to the adsorption of a layer of ions at the solid surface, which causes the ions in the liquid to redistribute. Although the existence of a layer of charges on a solid surface is always assumed, the origin of the charges is not extensively explored. Recent studies of contact electrification (CE) between a liquid and a solid suggest that electron transfer plays a dominant role at the initial stage for forming the charge layer at the L-S interface. Here, we review the recent works about electron transfer in liquid-solid CE, including scenerios such as liquid-insulator, liquid-semiconductor, and liquid-metal. Formation of the EDL is revisited considering the existence of electron transfer at the L-S interface. Furthermore, the triboelectric nanogenerator (TENG) technique based on the liquid-solid CE is introduced, which can be used not only for harvesting mechanical energy from a liquid but also as a probe for probing the charge transfer at liquid-solid interfaces.



Review

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1. INTRODUCTION

Contact electrification (CE) is a universal phenomenon that occurs for almost all solid materials. CE is the scientific term of triboelectrification, which is a combination of fractioning and CE. The nature of transferred charges in CE for solid materials has been debated for decades as being electrons¹⁻⁴ ions⁵⁻⁸ and even materials species 9^{-11} without a conclusive result. Recently, a nanoscale study using Kelvin probe force microscopy (KPFM) and a thin-film study using a triboelectric nanogenerator (TENG) suggested that the contact charge transfer in the solid-solid case is largely dominated by electron transfer.¹²⁻¹⁴ In these studies, the triboelectric charges were demonstrated to be removed from the dielectric surfaces by photon excitation and thermal excitation. Related physics models have been proposed for cases such as dielectric-dielectric and metaldielectric. Actually, when two materials are in contact with each other and then separated, charges will transfer from one surface to the other. CE can occur at almost all solid–solid, $^{15-19}$ liquid–solid, $^{20-23}$ and liquid–liquid $^{24-26}$ interfaces and may also at solid-gas and liquid-gas interfaces (Figure 1).

Charge transfer at the liquid–solid interface is a topic of broad interest and importance in chemistry, especially in electrochemistry, $^{27-32}$ catalysis, $^{33-37}$ etc., in which most chemical

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Figure 1. Schematic of the contact electrification between different phases. CE can occur at almost all solid–solid, liquid–solid, and liquid–liquid interfaces and may also at occur solid–gas and liquid–gas interfaces.

reactions occur at the liquid–solid interface. Many physical and biological phenomena are also related to charge transfer at the liquid–solid interface, such as electrowetting,^{38–41} colloidal suspension,^{42–45} photovoltaic effect,^{46–49} photosynthesis,^{50–52} etc. The fundamental sciences related to studies in above fields have been developed for decades but are mainly focused on some specific liquid–solid interface systems, such as the TiO₂– water interface, which is one of the key topics in water splitting.^{53–55} In contrast, liquid–solid CE concerns almost all liquid–solid interfaces. Therefore, it is of general significance to understand the charge transfer at the liquid–solid interface from the view of liquid–solid CE.

This review provides a summary about recent studies on the charge transfer at the liquid-solid CE. Besides ion transfer at the interface that has been set for decades, electron transfer is found to play a dominate role in some cases. First, a series of experiments with different observation techniques in both microscale and large scale has been systematically introduced to clarify the mechanism of electron transfer at the liquid-solid interface. Second, based on existing studies, formation of the electric double layer (EDL) is revisited owing to the contribution from electron transfer in liquid-solid CE, and a hybrid EDL model with a two-step formation process is proposed in which both electron transfer and ion adsorption are taken into consideration. Third, the applications of CE at the liquid-solid interface using the TENG as an energy harvester, sensor, chemical reactor, and so on, are systematically summarized. Finally, the impacts of electron transfer and the hybrid EDL model on applications of electrochemistry storage, interfacial reaction, EDL electronics, and many other research fields that relate to liquid-solid charge transfer are further discussed.

2. BRIEF HISTORY ABOUT STUDYING LIQUID-SOLID CE

The CE for a solid–solid interface has been known for more than 2600 years, but its mechanism has remained under debate until very recently.⁵⁶ When it comes to the liquid–solid CE, there are two basic issues. A core problem in liquid–solid CE is the identity of the charge carriers, and the other is the formation of the EDL. In the studies about electrochemistry,^{57,58} catalysis,⁵⁹ and colloidal suspension,^{60,61} the identity of the charge carriers and formation of the EDL are important. It was suggested that the charge transfer at the liquid–solid interface may be due to adsorption of ions in the liquid on the solid

surface^{62,63} or electron transfer from the liquid side to the solid side, which is accompanied by chemical reactions.^{64–66} Electron transfer is generally considered when the solid is a conductor or semiconductor. In addition, the adsorption of ions is traditionally considered to be responsible for the generation of charge transfer at the liquid–solid interface when the solid is an insulator. For the EDL, traditional studies focused on the distribution of ions and the structure of water molecules on the liquid side,^{67–69} and the fundamental study of the identity of the charge carriers on the solid surface in the EDL is a forgotten corner in general chemistry, possibly due to the lack of proper techniques.

In the history of studying the CE, most works focused on solid-solid cases, and the liquid-solid CE was not concerned.⁷⁰⁻⁷⁵ Therefore, the mechanism of liquid-solid CE is more mysterious than that of solid-solid CE. In the 1980s, El-Kazzaz and Rose-Innes et al. investigated the CE between liquid metals and solid insulators, which is one of the early works about the liquid-solid CE.⁷⁶ The purpose of using liquid metal as a contact pair is to take advantage of the fluidity of the liquid metal to create a better contact at the interface and further achieve a better understanding of solid-solid CE; therefore, it is not representative in liquid-solid CE. The CE between an aqueous solution and a solid is of concern in most cases. In the 1990s, Matsui and Yatsuzuka et al. studied the electrification phenomena between a water droplet and an insulator sur-⁷⁻⁷⁹ It was demonstrated that the water droplet is always face." positively charged when it slides over an insulator surface, such as PTFE and resin. Further, the position of the water in the triboelectric series was quantified by Burgo et al. in 2016.⁸⁰ In the above works, the adsorption of negative ions from water to the insulator surface is considered to be responsible for the contact charging between the water and the insulators. In fact, once the water is involved in CE, even in solid-solid CE, ion transfer was always assumed to be responsible for the CE^{6,81,82} but without solid proof.

Different from the CE between a solid and a solid, the identity of the charge carriers in liquid-solid CE has been assumed to be ions simply because of the involvement of the solution, but this fundamental assumption in the liquid-solid CE was not even verified experimentally. However, recent detailed studies available owing to the invention of liquid-solid triboelectric nanogenerators (L-S TENGs).⁸³⁻⁹⁴ The L-S TENGs were developed to convert mechanical energy into electricity based on the effect of liquid-solid CE, and it has re-excited researchers' interest in liquid-solid CE. Very recently, the identity of the charge carriers in liquid-solid CE was revisited.⁹⁵⁻⁹⁷ We investigated the liquid-solid CE at both the nanoscale and the macroscale. The data suggest that both electron transfer and ion transfer occur in the liquid-solid CE, and the electron transfer may even play a dominate role in some cases. The key to distinguish whether the transferred charges are ions or electrons can be done by two approaches: a temperatureinduced electron thermionic emission^{13,98} and an UV lightinduced electron emission,¹⁴ simply because neither approach could release the adsorbed ions on the surface if the temperature is moderate. Experimentally, we found that the charges on the solid surface generated by liquid-solid CE can be emitted by thermal excitation, which implies that electron transfer does exist in liquid-solid CE.⁹⁵ In addition, it was calculated that the number of ions in deionized water (DI water) is not enough to generate the observed charge density in liquid-solid CE.⁹⁶ On the basis of the electron transfer in liquid-solid CE, a "two-step"



Figure 2. Traditional model for the EDL. (a) EDL on the electrode surface. (b) EDL on the ionized solid surface. Ion distribution near the surface can be illustrated as a stern layer and a diffuse layer.



Figure 3. Temperature effect on the contact electrification between DI water and SiO_2 .⁹⁵ (a) Setup of the contact charge experiment. (b) Setup of the AFM platform for the thermionic emission experiments. (c) Charge density on the SiO_2 surface in the charging and heating cycle tests. Reproduced with permission from ref 95. Copyright 2020 Nature Springer.

model about the formation of the EDL was first proposed by Wang et al., in which the electron transfer plays a dominant role in the first step. 56

In summary, liquid-solid CE was not fully discussed in early studies, it was assumed that the charge carriers in liquid-solid CE were ions, and electron transfer was not even considered. Due to the invention of L-S TENG, the mechanism of liquidsolid CE has been revisited recently. It was suggested that electron transfer exists in liquid-solid CE. Moreover, a "twostep" model is proposed in which electron transfer between liquid molecules and solid surface atoms is the initial step and is followed by ion transfer due to electronic interaction.⁵⁶ The two-step model provides a new way to understand the formation of the EDL, which may have a significant impact on fundamental chemistry and even biology.

с



Cation ○Anion ● Electron ○Hole

Figure 4. Temperature effect on the contact electrification between DI water and different insulator surfaces: 95 (a) MgO, (b) Si₃N₄, (c) SiO₂, (d) HfO₂, (e) Al₂O₃, and (f) AlN. As for ion adsorption, both physical adsorption and chemical adsorption are possible, and they can be quantified using the method introduced by Lin et al. Reproduced with permission from ref 95. Copyright 2020 Nature Springer.

3. MODEL OF A TRADITIONAL ELECTRIC DOUBLE LAYER

As a central issue in electrochemistry, the model of the EDL is commonly utilized to discuss the charges and potential distribution at the liquid-solid interface. The concept of EDL was first proposed by Helmholtz,99 who discovered that two layers of opposite charges with a small distance formed at the electrode/electrolyte interface. This EDL model was then modified by Gouy and Chapman,^{100,101} who proposed that the ions are not closely attached on the solid surface but distributed in a thin layer region. In 1924, Stern¹⁰² combined the Helmholtz model with the Gouy-Chapman model and introduced the concept of two different regions of charges: the Stern layer and the diffuse layer, as shown in Figure 2a. The Stern layer (SL) is formed by the ions (often hydrated) strongly adsorbed on the charged electrode, and the diffuse layer (DL) is related to the concentration of ions (with opposite polarity to that of the electrode) that decreases with distance away from the surface. The Gouy-Chapman-Stern EDL model has been widely adopted in many fields, including electrolyte capacitors, ¹⁰³ electrochemistry reactions, ¹⁰⁴ capacitive deionization, ^{105,106} electric double-layer transistors, ¹⁰⁷ and electrowetting. ^{108,109} In Figure 2a, an external field is applied on the electrode to induce an EDL and the formation of the EDL on the surface of a precharged insulator is similar to the case of an electrode with an applied field. Meanwhile, when entering the double layer, the ions with a weaker solvation shell usually give away part of their solvation shell and only some solvated ions with a strong solvation shell (such as fluoride) can be held in position by purely electrostatic forces (see Figure 2a). On the basis of conventional EDL theory,¹⁰⁹ the chemical interaction between

half-solvated anions and the electrode surface can induce more charges on the electrode. and then countercharges are attracted to the double layer for charge compensation. In this case, for a solid material with abundant chemical groups, the EDL can also be formed due to the ionization or dissociation between the solid surface and the liquid. For example, a carbon material with carboxylic groups (-COOH) can attract counterions, which are decorated with abundant ionized groups (for example, -COO-), as illustrated in Figure 2b. This EDL picture is commonly used in colloidal science,¹¹⁰ cell biology, as well as capacitive mixing.^{111,112}

4. CONTACT ELECTRIFICATION AT THE LIQUID–SOLID INTERFACE

4.1. Liquid–Dielectric Interface

Decay of the tribo-charges on the insulator surface induced by thermionic emission was demonstrated as an approach that can be used to distinguish electron transfer from ion transfer in solid—solid CE.^{13,98} On the basis of thermionic emission theory, Lin et al. designed temperature-dependent charge decay experiments at the nanoscale using Kelvin probe force microscopy (KPFM) to quantify electron transfers and ion transfers in the CE between aqueous solutions and insulators.⁹⁵ In the experiments, the initial surface charge density of the insulator samples, such as SiO₂, Si₃N₄, MgO, etc., was measured using KPFM. Then, an aqueous liquid droplet slid over the insulator surface in this process. As shown in Figure 3a, the charges on the insulator surface generated in the liquid—solid CE could be electrons or ions. The ions are produced by



Figure 5. Squeezing system for studying liquid–solid contact electrification.⁹⁶ (a) Squeezing–recovering process of a droplet. (b) Amount of charge on deionized water (50 μ L) after being in contact with the PTFE membrane, and theoretical calculation based on the ion transfer model. Here, the experimental result is 10 times larger than the calculated value. (c) ¹H NMR spectrum of PTFE. (Insert) ¹H NMR spectrum of HCl solution (5 mol L⁻¹). (d) CE induced charge generation between water (HCl) and PTFE film. Reproduced with permission from ref 96. Copyright 2020 Wiley.

ionization reaction on the oxide and nitride surfaces.^{113–117} After the CE, the insulator sample was heated to a certain temperature (such as 513 K) and the electrons were thermally excited and emitted from the insulator surface according to thermionic emission theory in CE, as shown in Figure 3b. However, for the ions, they formed covalent bonds with the atoms on the insulator surface, which corresponds to chemical adsorption instead of physical adsorption. For ion chemical adsorption on the solid surface, such as OH^- and H^+ on the SiO_2 surface, the energy threshold for removing the OH^- from the SiO_2 surface is about 8.5 eV,¹¹⁸ and it is about 20 eV for removing H^+ .¹¹⁹ Therefore, the ions chemically adsorbed on the surfaces are quite hard to remove from the surfaces when the temperature is not too high.

Figure 3c gives the results of the charging and heating cycle tests. The initial surface charge density of the SiO_2 was close to zero. When it was in contact with DI water, negative charges transferred from the DI water to the SiO_2 surface. In the heating process (at 513 K and maintained for 10 min), the surface charge density decreased due to the thermionic emission of electrons. In the first cycle, it is noticed that some charges cannot be

removed from the surface ("sticky" charges), which can be identified as ions generated on the surface in the liquid-solid CE. In the flowing cycles, the sticky charge density increased and reached saturation eventually. This is because the available charge positions on the insulator surface are limited considering the breakdown field. When an ion is attached on the surface, an available charge position will be permanently occupied. In the next cycle of contact charging with DI water, both the electrons and the ions will transfer to the surface, but the number of transferred electrons will decrease due to the decreasing available charge position. Therefore, the removable charges on the insulator surface decreased with increasing test cycles. Though the ions are accumulating on the surface, the electron transfer was demonstrated to play a dominate role in the CE between a virgin SiO₂ surface and DI water in the very first contact; the ratio of electron transfers to ion transfers was more than 3.4.

Figure 4 shows the temperature effect on the CE between DI water and different insulators. The charge density on the insulator surface was found to decay exponentially, which is consistent with thermionic emission theory. For some materials,



Figure 6. Sliding-type TENG for studying the continuous electrification process between the liquid and the solid surface. 97 (a) Sliding motion of the droplet on the PTFE surface. (b) Charge saturation process on the PTFE surface. (Inset) Detailed charge transfer process at the beginning state and saturated state. (c) Soaking experiments, where the PTFE surface was previously immersed in different liquids before the electrification test. Reproduced with permission from ref 97. Copyright 2021 American Chemical Society.

the surface charge density became more positive, which implies that the solid received electrons in the CE (Figure 4a and 4c). In addition, some solids received holes, such as Si_3N_4 , HfO₂, Al₂O₃, and AlN. It is easy to understand that the negative charge density (SiO_2) or positive charge density (Si_3N_4, HfO_2) decreased with time at high temperature. This is because the negative charges on the solid surface are electrons and negative ions, and the positive charges are holes and positive ions. The electrons and holes were emitted at high temperature and resulted in a decay of the surface charge density. It is surprising that the charge density on some materials increased with decay time, such as MgO and Al_2O_3 ; this implies that the solids can receive both electrons and positive ions (MgO) when they come in contact with DI water or both holes and negative ions (Al_2O_3) . These results imply that electron transfer and ion transfer in liquidsolid CE are independent of each other. Moreover, the electrons and ions generated in the liquid-solid CE may be segregated at different surface areas.

In addition to KPFM, many other experimental methods have been applied to study the CE on the liquid-solid interface, and TENG is one of the powerful techniques for this purpose. Nie et al. designed a squeezing system to clarify the electrification performance between a liquid and a solid. The polytetrafluoroethylene (PTFE) membrane was used as the solid material, since it is quite stable with acid or alkali solutions.⁹⁶ The liquid droplet is located between two FTO-PTFE substrates, and the squeezing motion of the substrate is precisely controlled by a linear motor. The detailed squeezing process of a DI water droplet is shown in Figure 5a, where the water spreads evenly and finally turns into a thin liquid film, leading to a large contact area between the liquid and the PTFE film. After the contactseparation process, the amount of charge on the DI water droplet (50 μ L) can be measured using an electric meter, as can be seen in Figure 5b. With an increase of the contact area, the induced charge amount on the droplet is increased. In order to

determine the contribution of electron transfer and ion adsorption, a simple calculation was performed based on a pure ion adsorption model, as can also be seen in Figure 5b. The thickness of the ion diffusion in the liquid side at the liquidsolid interface is estimated to be ~20 nm. Generally speaking, this diffusion region for hydroxide ions is typically from a few Angstroms to tens of Angstroms.^{120,121} Moreover, the contact period for PTFE and a droplet is controlled to be smaller than 2 s, which is not enough for the diffusion of free ions into the deeper region. A value of 20 nm is ideal for maximizing the possibility of ion adsorption in the ideal case. Many suppression factors, such as the inhibition effect from the hydrogen ions (H^+) , are neglected in the calculation. A comparison between the experimental results and the calculated results in Figure 5b suggests that the ion transfer process may only provide 10% of the total charges. Therefore, the electron transfer process must be considered during the CE between water and PTFE.

In order to verify possible ion adsorption on the PTFE surface, a solid-state ¹H nuclear magnetic resonance (NMR) spectrometer was applied to measure the change of H elements after CE, as can be seen in Figure 5c. The same peak signal that appears at the same location (about 0.7 ppm) in all five spectra is related to the primary alcohol ethoxylate (AEO, RO- $(CH_2CH_2O)_nH)$ in the PTFE dispersion. The ¹H signal of water appears near 4.8 ppm,¹²² and the signals in the ¹H NMR spectra have a similar peak value after being in contact with deionized water, NaCl solution, and NaOH solution. However, the amount of charge transfer after being in contact with DI water is much larger than those with NaCl solution and NaOH solution,⁹⁶ indicating that the ion adsorption model cannot fully explain the CE between water and PTFE. Meanwhile, the signal from PTFE shows a large peak near 6.2 ppm after being in contact with HCl solution, which is caused by a chemical shift relative to water, and this is also related to the large amount of adsorption of H⁺ ions on the surface. When the acid solution is



Figure 7. Research strategy for using TENG as a probe to study charge generation on the liquid–solid interface.^{86,97,123,124} Reproduced with permission from ref 86. Copyright 2014 American Chemical Society. Reproduced with permission from ref 97. Copyright 2021 American Chemical Society. Reproduced with permission from ref 123. Copyright 2015 Wiley. Reproduced with permission from ref 124. Copyright 2019 Nature Springer.

in contact with PTFE, electron transfer and hydrogen ion adsorption occur simultaneously, but a high concentration of hydrogen ions is adsorbed on the surface of the PTFE to suppress electron transfer between the water molecules and the PTFE. These NMR spectra are in good agreement with the proposed model in Figure 5d.

Zhan et al. designed a sliding-type TENG to study the electron transfer on the polymer-liquid interface as shown in Figure 6a, which can further reveal the dynamic interaction between the droplet and the solid surfaces.⁹⁷ Here, PTFE film is also used for contact electrification, and water droplets can easily slide off an inclined PTFE film surface. As demonstrated in Figure 6a, the droplet first spread to a cone-like shape and then slid down the surface until it detached from the end. The induced charges from the interaction between DI water droplets and fresh PTFE polymers are continuously recorded, as shown in Figure 6b. On the basis of the working mechanism of TENG,⁹⁷ the electrostatic screening effect of the droplet on the charged surface can neutralize the charges on the overlapped region, which also leads to a current in the external circuit. Hence, the induced tribo-charge amount on the droplet can be decided by the difference between two charge transfer processes (contact and separation). The charge saturation effect on the PTFE surface can be revealed by checking the charge amount on each droplet. For the first droplet, a charge amount of 0.2 nC (Figure 6b) is observed when the droplet first contacts the polymer surface, which is due to the screening effect of the droplet. Then, as the droplet slides out of the surface, a charge amount of 2.6 nC (negative charge) is recorded, indicating that a

negative amount of charge of 2.4 nC (the difference between two signal) is induced on the PTFE surface due to the CE effect. On the other hand, with increasing droplet number, the accumulated negative charges on the polymer surface reach a saturation state. As shown in Figure 6b, during the saturation stage, the induced charges on the droplet remain constant, which is about 1 nC after about 80 droplets. It is also necessary to point out that even though the generated tribo-charges on the droplet is quite small, the screening effect of the droplet is quite strong at the saturation state; as can be seen in Figure 6b, a notable current can be generated for energy harvesting. Therefore, the charge curve in Figure 6b is like a square wave, and the total charge on the surface is approximately 51 nC.

A series of "soaking-dropping" experiments was conducted to clarify the contribution of the electron transfer effect, where PTFE films are soaked in different solutions to fully adsorb ions before water droplets are applied. In this case, the initial state of the PTFE surface may change due to the maximized process of ion adsorption. As can be seen in Figure 6c., the saturated charges (for 250 droplets) of the base-treated PTFE are about 70% of the original PTFE (untreated sample), which means that CE still occurred between water and treated polymer films. If ion adsorption is the dominating effect for the CE between the liquid and the solid, this soaking treatment should largely decrease the saturated charge amount on the PTFE surface. However, the results in Figure 6c show that the soaking treatment only has a limited influence in this experiment. Therefore, the CE in this experiment may be related to the hybrid effect of both ion adsorption and electron transfer.



Figure 8. DFT studies on the liquid–solid CE.¹³⁰ Different calculation models: (a) diamond carbon–water, (b) SiO_2 –water, (c) TiO_2 –water, and (d) HfO_2 –water. Normalized electron numbers of the valence band for (e) diamond carbon, (f) SiO_2 , (g) TiO_2 , and (h) HfO_2 in contact with water and solution. Normalized electron numbers near the Fermi level for (i) diamond carbon, (j) SiO_2 , (k) TiO_2 , and (l) HfO_2 in contact with water and solution. (m) Linear correlation between charge transfer and dielectric function that is based on introduction of the pinning factor. (n) Effects of dielectric constant and work function on the charge transfer at liquid–solid interfaces. Reproduced with permission from ref 130. Copyright 2021 Nature Springer.

On the basis of these experiments, the working mechanism of TENG is found to be quite suitable to study the physical processes at a liquid-solid interface, where the TENG device can work as a probe for detecting the charge generation and immigration (see Figure 7). Tang et al. first reported a liquidmetal-based TENG, which is aiming at high power generation through full contact between the metal and the dielectric.¹²³ Usually, TENG relying on solid materials cannot achieve 100% contact considering the roughness of the surfaces. Thus, application of liquid metal can solve this problem, where a high output charge density of 430 μ C m⁻² and a power density of $6.7 \text{ W} \text{ m}^{-2}$ can be achieved with this kind device. This idea was then developed into a kind of probe method for determining the electrification series of different dielectric materials. Zou et al.¹²⁴ introduced a standard method to quantify the triboelectric series for various polymer materials, which is based on contact

electrification between the tested materials and a liquid metal. The proposed method employed TENG as a charge probe for uniformly quantifying the surface charge density of general materials, which can reveal the intrinsic nature of the polymers for gaining or losing electrons. In addition to liquid metal, the similar TENG system can also be applied to studying the electrification capability of different liquids, as we introduced in the last section.⁹⁷ Figure 7 also illustrates a TENG array for detecting the dynamic output during the sliding motion of a droplet on a solid surface, and this kind of design can show the detailed interaction between the liquid droplet and a large solid surface. This kind of single-electrode-type TENG has very high sensitivity for detecting the induced charge on the liquid-solid interface,¹²⁵ and the calibrated charge amount can reach pC scale. Moreover, combined with high-speed video, the dynamic electrical outputs of TENG at variable impact conditions allow



Figure 9. Tribovoltaic effect at the liquid–semiconductor interface. 136 (a) Setup of the tribovoltaic experiments and external circuit. (b) Oscillogram of tribo-current when a DI water droplet slides on the P-type silicon wafer. (c) Generation of the "bindington" at the sliding water and semiconductor interface. (d) Energy band diagram of the tribovoltaic effect at a liquid–solid junction. Reproduced with permission from ref 136. Copyright 2021 Elsevier.

us to describe the electrical response quantitatively without any fit parameters.¹²⁶ It is possible to derive many scaling laws for liquid–solid electrification by matching the evolution of the hydrodynamic spreading process and the time scales of the external electrical signal. A similar application of TENG as a charge probe can also be done using different modes of TENGs, such as free-standing-type TENG¹²⁷ or even liquid-membranetype TENG,²⁴ where TENG can work as a sensor or electrostatic charge filter to precisely measure the surface charges on the targeting object. Hence, due to its high sensitivity and diversified structure design, TENG is a powerful technique for studying the electrical interaction between liquids and other objects, while much progress can be expected in the near future.

In addition to experimental studies, some theoretical calculations also support the fact that electron transfer can occur at the liquid-insulator interface. Willatzen et al. developed a quantum-mechanical model for predicting the electron transfer in the CE for different materials systems, including liquid-solid cases.¹²⁸ In the quantum-mechanical model, ion transfer was not considered but electron transfer seems to be sufficient to support the CE between the liquid and the solid CE. Li et al. investigated the CE between a metal and amorphous polymers when the water layers exist at the interface using the first-principles method.¹²⁹ The results show that electrons will transfer at the metal-water layer interface and polymer-water layer interface. Very recently, Sun et al. quantified the electron transfer in the liquid-solid systems in different oxides based on density functional theory (DFT).^{130,131} Different liquid-solid systems were established in which the solids were diamond carbon, dielectric insulator



Figure 10. Tribovoltaic effect at the liquid—metal interface. (a) Energy band diagram at a liquid—solid junction before contact and in contact. (c) First-principles calculations about the electron transfer at the water and Pt interface.¹³⁹ Reproduced with permission from ref 139. Copyright 2018 Royal Society of Chemistry.

(SiO₂), and metal oxides (TiO₂ and HfO₂) and the liquid was water, as shown in Figure 8a-d. The total density of states (TDOS) of the liquid-solid interfaces was used to evaluate the charge transfer behavior. In addition, the Na ions were introduced in the liquid-solid interfaces to investigate the effect of the ionic solution concentration on the liquid-solid CE. Two different calculations show the electron transfer in the valence band of the solid (VB). The first was the electron number changes in the whole VB of the solids, and the other was the electron number changes in a small range near the Fermi level. Figure 8e-1 shows the normalized electron number changes in the whole VB and that in a small range near the Fermi level when the solids contact the water or ionic solutions. The charge transfer between the aqueous solution and different solids was demonstrated to be related to the changes of the vacuum level and Fermi level of the solid surface when it comes in contact with the aqueous solution. In addition, it is proved that the Na ions enable the band offset, leading to the change of the liquid-solid electron transfer. Furthermore, a linear relationship between liquid-solid electron transfer and the dielectric function was found (Figure 8m). In addition, the effects of the dielectric constant and work function of the solid surfaces on charge transfer are shown in Figure 8n. The DFT studies proved that the liquid-solid CE is a complicated phenomenon, which can be affected by the contact angle, dielectric function, temperature, and ion concentration, etc. It needs to be mentioned that all of these first-principles calculations were based on electron transfer, which is consistent with the experimental work on electron transfer in CE.

4.2. Liquid–Semiconductor Interface

Recently, the solid–solid CE involving semiconductors was found to generate current directly with a high current density.^{132–134} Wang et al. pointed out that the generation of direct current at the semiconductor interfaces is similar to what occurs with the photovoltaic effect.⁵⁶ When a P-type semiconductor slides over a N-type semiconductor, the released energy "quantum" will be released at the interface due to the formation of new chemical bonds. The released energy can excite electron–hole pairs at the interface, which are further separated and moved from one side to the other side under the built-in electric field at the semiconductor interface, generating direct current in an external circuit. This phenomenon is analogous to the photovoltaic effect and called the "tribovoltaic effect".

The photovoltaic effect can occur not only at the solid-solid interface but also at the aqueous solution and solid semiconductor interface, in which the aqueous solution is considered as a liquid semiconductor. $^{46-49,135}$ This implies that the tribovoltaic effect may also occur at the aqueous solution and solid semiconductor interface, since the tribovoltaic effect is similar to the photovoltaic effect. As shown in Figure 9a, Lin et al. used a syringe conductive needle to drag a DI water droplet to slide over a silicon surface.¹³⁶ Figure 9b shows the short-circuit current between the conductive needle and the P-type silicon wafer. The positive current was found to be generated when a DI water droplet slides over the P-type silicon surface, which implies that the electrons moved from the P-type silicon side to the DI water side at the interface. When the DI water droplet slid on the N-type silicon surface, a negative tribo-current was generated and the electrons moved from the N-type silicon side to the DI water side at the interface. The direction of the tribocurrent was found to be consistent of the direction of the built-in electric field at the water and silicon interface. Further, Zheng et al. investigated the tribovoltaic effect at the liquid-solid interface under light irradiation.¹³⁷ It was revealed that the tribo-current between DI water and the silicon wafer can be significantly enhanced by light irradiation, due to an increase of the electron-hole pairs at the interface. These studies proved that the tribovoltaic effect can occur at the liquid-solid interface.

In the liquid—semiconductor tribovoltaic effect, the energy to excite the electron—hole pairs is also considered to come from the formation of the chemical bond at the interface. As shown in Figure 9c, when a water droplet slides over a semiconductor surface, some water molecules will come in contact with the fresh surface, forming chemical bonds and releasing energy, and the released energy "quantum" is called "bindington". Figure 9d gives the whole process of the tribovoltaic effect at the liquid—solid interface. When a liquid and a solid semiconductor come in contact with each other, the built-in electric field will exist at the interface due to the difference in the Fermi levels. If the liquid starts to slide on the solid semiconductor surface, the bindington

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Figure 11. Wang transition model for contact electrification.^{56,98} Interaction of two atoms at the (a) equilibrium position, (b) attractive position, and (c) repulsive position. Schematic of the energy diagram of two atoms (d) before contact and (e) in contact; photon emission is observed experimentally due to the hopping of electrons. Reproduced with permission from ref 56. Copyright 2019 Elsevier. Reproduced with permission from ref 98. Copyright 2019 Wiley.

will be released and electron-hole pairs will be excited at the interface. Driven by the built-in electric field, the electron-hole pairs are separated and move from one side to the other side, generating a continuous direct current in external load.

Though the mechanism of the tribovoltaic effect at the liquid-semiconductor is different from that of the CE between the liquid and the insulator surface, the charge carried in the tribovoltaic effect is also electrons, which implies that the tribovoltaic effect at the liquid-solid interface also supports the "two-step" model for the formation of the EDL, in which the electron transfer between the liquid and the solid is the first step.

4.3. Liquid-Metal Interface

In the tribovoltaic effect at the DI water and silicon interface, the DI water is considered as a semiconductor. This means that the junction between the DI water and silicon corresponds to a PN heterojunction. In solid–solid cases, the tribovoltaic effect was demonstrated to exist not only in PN junctions but also in Schottky junctions, which are usually at the semiconductor–metal interfaces.¹³⁸ Therefore, the tribovoltaic effect should also exist at DI water and metal interfaces, which correspond to the Schottky junctions. As shown in Figure 10a, the Fermi level of the metal is lower than that of DI water. When they come into contact, a built-in electric field will be established to compensate for the difference in the Fermi level (Figure 10b). In the Schottky junctions, the depletion region is always at the

semiconductor side in the solid—solid case. This suggests that the depletion region should be in the DI water side in the DI water—metal junction, which implies that the EDL at the metal and DI water interface can be considered as the depletion region in liquid—metal cases. Recent experimental works have proven that the tribovoltaic effect also exists at the metal and DI water interface.

In addition to the tribovoltaic effect, in which the transferred electrons are from the excited electron—hole pairs, charge transfer in the traditional sense can also occur between metals and liquids. As shown in Figure 10c, the first-principles calculations show that when the water comes in contact with a metal surface, such as Pt, the electron will directly transfer from one side to the other at the interface.¹³⁹ The charge transfer at the water—metal interface is of significant interest not only in liquid—solid CE but also in studies on corrosion and catalysis, etc., in which charge transfer is a fundamental issue. In both the tribovoltaic effect and the direct charge transfer at the liquid—metal interface, the charge carriers are identified to be electrons when a metal is involved.

5. "WANG TRANSITION" FOR CONTACT ELECTRIFICATION

The above work demonstrated that electron transfer plays a dominate role in the liquid—solid CE, which raises the following



Figure 12. Application of L–S TENG for energy harvesting. (a) Energy collection on a large surface.^{149,150} Reproduced with permission from ref 149. Copyright 2016 Elsevier. Reproduced with permission from ref 150. Copyright 2017 Elsevier. (b) Portable and wearable energy package,^{156–158} Reproduced with permission from ref 156. Copyright 2020 Royal Society of Chemistry. Reproduced with permission from ref 157. Copyright 2017 Wiley. Reproduced with permission from ref 158. Copyright 2018 American Chemical Society. (c) Hybrid power source.^{160,161,164,165} Reproduced with permission from ref 160. Copyright 2021 Elsevier. Reproduced with permission from ref 161. Copyright 2015 Wiley. Reproduced with permission from ref 164. Copyright 2019 American Chemical Society. Reproduced with permission from ref 164. Copyright 2019 American Chemical Society. Reproduced with permission from ref 165. Copyright 2020 Reproduced with permission from ref 164. Copyright 2020 Elsevier.

question: what are the conditions for electron transfer in CE? The Wang transition model for contact electrification provides answers to this question.⁹⁸ As shown in Figure 11a, there is a distance between atom A and atom B that keeps the two atoms in equilibrium. When the distance between the two atoms is larger than the equilibrium distance, they will attract each other (Figure 11b). On the contrary, if the distance between the two atoms is smaller than the equilibrium bonding distance, the electron clouds of the two atoms will overlap and will repel each other (Figure 11c). On the basis of the experimental data, Wang et al. pointed out that the electron transfer in CE can only occur when the electron clouds of the two atoms overlap.⁹⁸ As shown in Figure 11d, the highest occupied energy level of the atom belonging to material A is higher than that of the atom belonging to material B. If the two surfaces are not in intimate contact, the electron clouds of the atoms belonging to the two surfaces do not overlap. The electrons will not transit from atom A to atom B in this case due to the high potential barrier between them. When the two surfaces are in intimate contact, the electron clouds of atom A and atom B overlap and reduce the potential barrier and the electrons will transit from atom A to atom B, which can be simply referred to as the Wang transition (Figure 11e). Here, the electrons can transit to any energy level of atom B that is below the highest occupied energy level of atom A. In addition, the electrons will further transit to the lowest unoccupied energy level of atom B and photons will be released, which has been observed experimentally. The overlap of electron clouds, which provides a pathway for electron transfer in CE, can be considered as forming a chemical bond with a much longer bonding length comparing to traditional chemical bonds. When the two surfaces are separated after contact, atom A, which loses electrons, will be dragged by the other atoms on the material A surface, the bond between the two atoms (atom A and atom B) extends in length and eventually breaks, and atom A will separate from atom B, resulting in CE. However, in some cases, the attraction force between atom A and atom B is stronger than that between atom A and the material A surface,

the bond between the two atoms (atom A and atom B) will become stronger, atom A will be left on the material B surface, forming a new real chemical bond, and chemical reaction occurs. In these cases, the CE cannot be detected, since a whole neutral atom transfers from surface A to surface B. The Wang transition model was verified by both experimental and theoretical studies. Lin et al. investigated the CE between the Pt coating and $Si_3N_4/$ AlN using tapping-mode AFM in a different interaction region of the tip-sample interaction force (repulsive or attractive).¹⁴⁰ It was found that the CE between the tip and the sample can only occur when the tip and sample interact in the repulsive region, which consistent with the Wang transition model. Willatzen et al. provided a first quantum-mechanical calculation for electron transfer between two dissimilar atoms. The results also shown that the overlap of electron clouds belonging to two contact atoms is a necessary condition for electron transition.¹⁴¹

The Wang transition model can explain CE in many cases, including liquid—solid cases. Owing to liquid pressure, the liquid molecules will collide with atoms on the solid surface at a liquid—solid interface. The collision between liquid molecules and the atoms on the solid surface may lead to the overlap of electron clouds and result in electron transfer. In some cases, the atoms, which receive/lose electrons from/on the solid surface, are dragged away from the solid surface by other molecules in the liquid. The transferred electrons are left on the solid surface, resulting in a traditional liquid—solid CE. However, sometimes the atoms belonging to the liquid molecules may form a new bond with the atoms belonging to the solid surface. In these cases, the bindington will be released; if the solid is a metal or semiconductor, tribovoltaic current will be generated.

6. LIQUID-SOLID CE-BASED TRIBOELECTRIC NANOGENERATOR

Contact electrification on the liquid—solid interface is actually a long-standing unsolved issue in the chemical—physical field, and this topic has recently drawn notable attention from researchers in many fields. One of the reasons for this situation is related to

the fast development of L-S TENG. Ambient water motions, including river flows, ocean waves, and even rain drops, contain tremendous mechanical energy, and TENG that can collect energy from these ambient water motions is a desirable technique for on-site energy demand. Traditional energyharvesting techniques rely on electromagnetic generators^{142,1} or piezoelectric generators that have their limitations for collecting energy from liquid-solid motions, such as a size limitation, complicated structure, or low conversion efficiency. Therefore, the TENG device, which have the advantages of a small size, simple system, low cost, and direct interaction with water bodies, can be a key technique to solve the problems in this area. The operation mechanism of L-S TENG, which is based on a combination of the electrification effect and the electrostatic screening effect, has been thoroughly studied in many previous works.^{83–94} The detailed difference between these two effects can also be seen in the results in Figure 6b. The electrification between the moving liquid and the solid surface is the fundamental element, while the design of the TENG structure is either single-electrode type or free-standing type. In 2013, Lin et al. reported the first L-S TENG,^{83,92} which is based on a single-electrode-type structure. Then, many other researchers developed a free-standing-type TENG for collecting energy mainly relying on the screening effect of the liquid.^{144,143} Last year, Wang et al. reported a new transistor-inspired L-S TENG device based on the bridge phenomenon between the electrification surface and an Al electrode.¹⁴⁶ In this device, the spreading of a water droplet on the electrification surface can bridge the conventional interfacial effect into a bulk effect, leading to a very high instantaneous power density. One hundred commercial LEDs can be powered by one droplet (100.0 μ L), which is so far the highest performance of L-S TENG. Hence, with the development of the fundamental study of S-L electrification, a series of new breakthroughs can also be expected in the near future. Moreover, Wang et al. also designed a novel slippery lubricant-impregnated porous surface-based TENG (SLIPS-TENG) to overcome fast degradation of the triboelectric properties of interfacial materials under harsh environments.^{147,148} SLIPS-TENG is now an emerging area of liquid-solid contact electrification, which eliminates many inherent challenges encountered in current TENG.

Currently, the design of L–S TENG for energy harvesting can be briefly divided into three categories, as shown in Figure 12. First, the L-S TENG can be applied for energy collection on a large surface (Figure 12a), such as windows, ¹⁴⁹ building walls, ¹⁵⁰ and so on. For example, Liang et al. developed a multiunit transparent TENG that can be directly applied on the window of a car, 149 where the instantaneous power density can reach 12.66 mW m⁻². Meanwhile, the L-S TENG investigated by Choi et al.¹⁵⁰ had a surface nanostructure based on the natural surface of lotus leaves. Relying on the fluorinated electrification surface with high hydrophobicity, this TENG can work for 28 days without performance degradation.¹⁵⁰ Zhong et al. proposed a multilayer L-S TENG with fine electrode arrays targeting at the droplet or stream energy,¹⁵¹ which can fully convert the gravitational potential energy into electricity. In addition to the raindrop, a similar L-S TENG can also be applied to collect energy from ocean waves and streams. The design of L-S TENG for water wave energy is almost the same as that for raindrop energy, where the free-standing electrode array should be utilized to generate continuous displacement current.

For the electrification surface of L–S TENG, the charge density and the hydrophobicity are two major parameters to

determine the performance of energy generation. Actually, the increase of the hydrophobicity does not always lead to an increase of the charge density. Many researchers have reported that an excessive increase of the roughness and the contact angle results in the suppression of transferred charges.^{152,153} For the hydrophobic materials, an increase of the surface roughness leads to high hydrophobicity, while it may also decrease the effective contact area between the droplet and the surface (the liquid cannot completely infiltrate the uneven surface on the microscale). On the other hand, the high hydrophobicity allows the liquids to smoothly move on the solid surface, while the current output from TENG is directly related to the motion velocity, suggesting that the high hydrophobicity is good for producing a high current signal. Hence, a suitable hydrophobicity (neither too high nor too low) is quite important for L-S TENG, and this value needs to be specially designed for different devices. Moreover, the charge injection treatment is another commonly used method to modify the electrification surface of L-S TENG.¹⁵⁴ The excessive charges are injected onto the solid surface by ion guns or corona polarization, while the energy generation relies on the electrostatic screening effect caused by the moving droplet (the solid electrification surface is always at the saturation state).¹⁵⁵ For the charge injection treatment, the solid material should be electret materials; otherwise, the surface charge density cannot be maintained during the operation. Thus far, a series of electret polymers has been applied for the study, including PTFE, FEP, CYTOP, and so on. Here, the surface charge density and its persistence after the injection treatment are decided by the polarity of the polymer molecules (the dipole moment, the density of the polar molecule, and so on). According to the previous reports, the CYTOP film with high-temperature polarization is for now the best option for this kind of L-S TENG.¹⁵

Second, portable and wearable energy packages are also a major research direction of L–S TENG, as can be seen in Figure 12b. Zhao et al. demonstrated a bielectrode freestanding that can be attached on the surface of am umbrella,¹⁵⁶ and this is a typical application of L-S TENG as a portable energy package. The generated output power density from this device can reach $1.838 \text{ W} \text{ m}^{-2}$, which is enough to light up 30 commercial LEDs, and this performance is the result from the device on a real umbrella. Besides umbrellas, rain coats and shoes are also suitable targets for integrating TENG. Xiong et al. reported a wearable all-fabric-based TENG which can work as a smart cloth to harvest energy from water flow.¹⁵⁷ Moreover, this fiber-based L-S TENG can achieve an additional function of bei g selfcleaning, where the hydrophobic nanoparticles are coated on various fabrics to serve as the electrification materials. The device can generate an instantaneous output power density of 0.14 W m⁻², while both the electrostatic energy and the mechanical energy of water can be collected by this L-S TENG. On the other hand, electrification on the S-L interface is usually deficient in comparison with the case of the solid-solid interface, especially when the device is completely immersed in the liquid. Accordingly, for the wearable L–S TENG devices, research is needed to further enhance the liquid-solid interactions by inducing more turbulence via designing microturbulators on the electrification surface¹⁵⁸ or by designing some tiny drainage channel on the electrification surface to increase contact-separation motions between the solid and the liquid.159

Third, a hybrid energy generator is an interesting and intensively studied research direction of TENG, which is aiming



Figure 13. Diversified applications of liquid–solid contact electrification in addition to energy harvesting.^{25,26,90,166–172} Reproduced with permission from ref 25. Copyright 2020 Elsevier. Reproduced with permission from ref 26. Copyright 2019 Wiley. Reproduced with permission from ref 90. Copyright 2019 Elsevier. Reproduced with permission from ref 166. Copyright 2016 Elsevier. Reproduced with permission from ref 167. Copyright 2019 Nature Springer. Reproduced with permission from ref 168. Copyright 2017 Wiley. Reproduced with permission from ref 169. Copyright 2018 American Chemical Society. Reproduced with permission from ref 170. Copyright 2018 Royal Society of Chemistry. Reproduced with permission from ref 171. Copyright 2015 Elsevier. Reproduced with permission from ref 172. Copyright 2015 American Chemical Society.

at collecting multiple types of energy from surrounding environments. L-S TENG has excellent performance for collecting energy from raindrops, and it can effectively work for the hybrid energy system (see Figure 12c). The advantage of L-S TENG is the universal applicability, which allows it to parallel work with many other types of energy harvesters. For example, Zheng et al. reported the first hybrid energy system based on a solar cell and L-S TENG,^{160,161} which can harvest the energy from both the sun and a raindrop. The transparent TENG is attached on the top surface of a solar cell, while the falling raindrop can induce energy output by contacting the TENG surface. Considering the low efficiency of a solar cell during rainy days, this hybrid system can compensate for the energy loss of the solar cell. Much progress has been made for this solar-raindrop energy system. For example, different nanopatterns have been applied on the TENG surface, which can further enhance the light absorption of the solar cell.^{162,163} Self-healing and self-cleaning materials have been employed for fabricating L-S TENG, while the light transparency and the long-term operation of the solar cell can be further protected.¹⁶⁰ In addition to solar energy, the L-S TENG can also work with wind energy harvesters. Ren et al. reported a self-adaptive TENG which can show spontaneous deformation with different humidity¹⁶⁴ (see Figure 16c). The humidity-sensitive material is integrated on the joint site of TENG, while the humidity change leads to the banding of TENG to different positions. On windy days with normal humidity, the TENG arrays all stand up and the vibration of these TENG arrays in the wind can generate electrical energy. Then, on rainy days, the high humidity in the air drives the TENG arrays to lay down and the electrification surface can harvest the raindrop energy based on the CE effect. Moreover, Jiang et al. proposed a hybrid generator consisting of a free-standing-type L-S TENG and a pyroelectric generator (PENG) for collecting both the thermal energy and the kinetic energy of the thermal fluids.¹⁶⁵ The output power of the TENG decreases with increasing droplet temperature, since the CE effect is related to ambient temperature. This hybrid energy harvester can achieve a peak power density of 2.6 μ W cm⁻², and a maximum energy increment of 238% in comparison with pure PENG device is also obtained, where 28 commercial LEDs can be lit up by this device. For the hybrid energy system, different

energy generators can be combined with the help of a rectifier circuit or storage units, where the unified energy density is higher than a single unit. Despite its diversity based on different physical effects and mechanisms, the cooperation method between different generator units still needs further exploration in order to simultaneously harvest different environmental energy and compensate for the drawbacks of each unit.

In addition to energy harvesting, electrification on the L-S interface also can serve as a force-electricity conversion effect and inspires many other applications, as partially summarized in Figure 13. A fluidic sensor for detecting motions and deformations is a major research direction relying on L-S electrification. For example, Shi et al. proposed a flexible pressure sensor based on L-S electrification in a microfluidic channel.¹⁶⁶ This sensor can conformably work on human skin with coupled working principles of electrification and capacitive changing. The electrification between the microfluidics and the channel surface can directly reveal the dynamic pressure without external power supply, while capacitive change is a complementary sensing mechanism to distinguish dynamic and static pressure. This microfluidic sensor can simultaneously monitor both the magnitude and the frequency of the pressure, which can be applied for complex human motion monitoring. A similar working principle can be applied for underwater wearable electronics. Zou et al. designed a bionic L-S TENG mimicking the ion channels in an electric eel, which can harvest energy from underwater motions.¹⁶⁷ The flowing liquid in the electrification channel leads to an output voltage of over 10 V, and the generated electricity can support body multiposition motion monitoring and an undersea rescue system. In addition to a fluidic motion sensor, electrification on the S-L interface can also serve as a surface chemical senor. Chen et al. reported a selfpowered volume sensor based on L-S CE,¹⁶⁸ which is capable of sensing both the volume and the electrical conductivity. Moreover, the ultrafine/highly flexible structure of this device enables its application for microliquid biological and chemical detection. Jiang et al. also reported an application of L-S TENG for identifying the concentration of the dopamine on the liquidliquid interfaces.²⁶ Moreover, the electrowetting technique can achieve fine control of both the position and the velocity of fluids in the microchannels. By combining the electrowetting



Figure 14. Wang's hybrid EDL model and the "two-step" process on its formation. (a) In the first step, the molecules and ions in the liquid impact the solid surface due to the thermal motion and the pressure from the liquid, which leads to electron transfer between them; meanwhile, ions may also attach to the solid surface. (b) In the second step, free ions in the liquid would be attracted to the electrified surface due to electrostatic interactions, forming an EDL.

technique and L–S electrification, various self-powered microfluidic systems can be realized. For example, Nie et al. designed a minivehicle using four droplets to carry a pallet, ¹⁶⁹ which can transport tiny objects with the highest controllable velocity of 1 m/s. Chen et al. also demonstrated that the induced electrical output from the electrification between a droplet and the TENG surface is enough to drive an electrowetting actuation matrix. ¹⁷⁰ Another promising application direction of L–S CE is related to corrosion protection for ships or ocean machines. The L–S TENG can support the sustainable corrosion protection process without using an external power source, ^{171,172} while mechanical energy can be easily obtained from ocean waves. Actually, a selfpowered sensor based on L–S TENG may have tremendous applications in ocean-related fields. For example, the level gauge based on L–S electrification can serve in various situations, such as cargo ships²⁵ or drilling platforms.⁹⁰

7. REVISITING THE MODEL OF THE ELECTRIC DOUBLE LAYER

7.1. Wang's Hybrid EDL Model and the "Two-Step" Formation Process

As introduced above, the electron transfer process is a strong effect that should not be neglected during the CE between the liquid and the solid, and thus, electron transfer should also be considered in the formation of the EDL. As can be seen in Figure 14, a hybrid EDL model (simply referred to as Wang's hybrid layer), which was first proposed by Wang et al.⁵⁶ in 2018, and a "two-step" process for the formation are elaborated with the consideration of both electron transfer and ion adsorption (chemical interaction), that is, in the first step, the molecules and ions in the liquid impact the solid surface due to the thermal motion and the pressure from the liquid, while the overlap of the electron clouds of the solid atoms and water molecules leads to the electron transfer between them (Figure 14a). For example, the solid materials with strong electron-capturing capability (such as polymers with a large number of fluorine groups) can directly obtain electrons from the water molecules and even ions

in the liquid. Then, due to liquid flow or turbulence, the liquid molecules that are adjacent to the solid surface can be pushed off of the interface. The electron transfer process is related to the hopping of electron from a high-energy state to a low-energy state. Hence, after separation, most of the electrons transferred to the surface can be maintained if the energy fluctuation of the electrons (kT), where k is Boltzmann's constant and T is the temperature) is lower than the energy barrier $(E_{\rm n})$. In the second step, free ions in the liquid would be attracted to the electrified surface due to electrostatic interactions, forming an EDL, which is similar to the traditional EDL model (Figure 14b). Meanwhile, the ionization reactions also occur simultaneously on the solid surface, while both electrons and ions are generated on the surface. In addition, when a water molecule loses an electron, it becomes cationic, H_2O^+ . The lifetime of H_2O^+ is proved to be less than 50 fs,¹⁷³ and it joins with a neighboring water molecule to yield an OH radical and H₃O⁺ based on the chemical reaction¹⁷⁴ $H_2O^+ + H_2O \rightarrow OH + H_3O^+$. Therefore, the severed molecules being pushed off the solid surface become freely migrating ions in the liquid, and these ions can also participate in the formation of the EDL.

There are several key points for this hybrid EDL model. First, the ions produced by the ionization reaction and the transferred electrons can both change the potential distribution near the surface, while formation of a Stern layer and a diffusion layer will not have an essential difference in this hybrid EDL model. In the traditional EDL model, the ionized interaction on the liquidsolid interface induces more charges on the surface, which results in the charge distribution and compensation in the diffusion layer. In the hybrid layer, the charge transfer between solid and liquid molecules causes even more charges to be accumulated at the surface. This electron transfer process works parallel with the ion adsorption process, and for some cases, the electron transfer plays a dominant role in the surface charge generation, such as the CE between SiO₂-water and PTFEwater.^{95,96} The adsorption of ions can be chemical adsorption and physical adsorption. Meanwhile, the different part of this



Figure 15. Revisiting the EDL and its related fields: (a) electrochemical storage,¹⁰³ (b) electrocatalytic system,¹⁷⁵ (c) mechanochemistry,¹⁸² (d) electrophoresis and surface adhesion,¹⁸⁵ (e) colloidal suspension,¹⁸⁶ and (f) EDL transistor.¹⁸⁸ Reproduced with permission from ref 183. Copyright 2002 Elsevier. Reproduced with permission from ref 189. Copyright 2018 American Chemical Society.

hybrid EDL model is related to the surface condition on the solids. The transferred electrons are usually trapped in the surface states, while the extra charges produced in the ionization reaction are trapped in the atomic orbitals of the atoms. Accordingly, the potential barrier of the surface states should be lower than that of the atomic orbitals, and the transferred electrons in the surface states are removable and relatively unstable, which is proved by the experiment using heating treatments.95 Moreover, the electron-donating/withdrawing capability of solid materials can determine the CE between solids, and this rule can also be applied to the CE between a L and a S.^{22,175} For example, the polymers with strong EW ability (PTFE and FEP) can generate a significant electron transfer effect during the CE with liquids, and the electrification performance can be further enhanced by deliberately increasing some unsaturated groups on the surface. Hence, the formation of the EDL, including the charge density and the potential distribution near the surface, may also be influenced by the electron-donating/withdrawing capability of solid materials. Furthermore, the probability of electron transfer in a liquidsolid CE is usually less than 1 out of \sim 2500 surface atoms.⁹⁵ For the case of CE between SiO₂ and DI water, the distance between two adjacent electrons on the SiO₂ surface is \sim 16 nm and the distance between two adjacent O^- ions is ~30 nm, which is estimated based on the charge density. These distances are much larger than the thickness of the Stern layer,¹⁷⁶ and the illustration of the EDL should also consider the distance of two adjacent charges, as shown in Figure 14.

7.2. Revisiting the Model of EDL and Its Related Fields

The EDL model has been widely adopted in many fields, including energy storage, electrochemistry reaction, capacitive deionization, hydrogel ionotronics, electrophoresis, colloidal adhesion, and so on. However, the electron transfer effect during the liquid-solid contact may bring out another origin for the formation of the EDL on the liquid-solid interface as we proposed in Figure 14. On the basis of this hybrid electrification process (electron transfer and ion adsorption) on the S-L interface, we suggest revisiting the study and the application related to the EDL, as can be seen in Figure 15. EDL capacitors¹⁰³ are replying to charge accumulation in the EDL to store energy (Figure 15 a), and the EDL behavior at the electrode surface is usually decided by the applied electrical field, the types of electrolyte ions, and the ion adsorption process. Then, the interaction between adsorbed ions and the electrode surface is explained based on the chemical affinity. If we consider the electron transfer between the electrode surface and the liquid molecule, we need to further consider charge accumulation and distribution near the surface. Even though the electron transfer effect is more significant on the polymer-liquid interface²² and is usually quite weak on the electrode-liquid interface, it is still necessary to consider this effect for completing the physical picture near the electrode surface. Previous work has demonstrated that self-discharge of EDL capacitors can be suppressed by introducing electrorheological liquid crystal molecules in the electrolyte, where the surface potential can induce fluid viscosity to decelerate the diffusion of ions.¹⁷⁷ This



Figure 16. Impact of the hybrid EDL model on other energy generators. (a and b) Energy harvesting from streaming current.^{145,191} (c) Energy harvesting from surface vapor evaporation.²⁰¹ Reproduced with permission from ref 191. Copyright 2015 Wiley. Reproduced with permission from ref 145. Copyright 2016 American Chemical Society. Reproduced with permission from ref 201. Copyright 2017 Nature Springer.

result also suggests that the electron transfer effect can make a unique contribution for some special cases. Similarly, the capacitive and pseudocapacitive processes of the EDL have been proved to have a significant impact on electrocatalytic reactions (Figure 15b),^{178,179} where continuous EDL reconstruction is observed due to chemical phase modification. The presence of the EDL and the electrified interface can be used to explain the influence of cations on the experimental performance,^{180,181} and definition of the local environment for catalysis also needs to include the electrostatic interactions of the ionic species with the charged metallic surface. In this case, the hybrid EDL model including the electron transfer process can also help to clarify some physical hypotheses based on experimental observations.

On the other hand, mechanochemistry is the study of the influences of mechanical force on chemical bonds of forceresponsive materials, which can possibly produce some new materials inaccessible by other means. For example, Boswell et al.¹⁸² synthesized a gold-colored, semiconducting fluoropolymer (fluorinated polyacetylene) using ultrasonication to produce force activation (Figure 15c), indicating that polymer mechanochemistry is a valuable synthetic tool for accessing unique materials. In this case, the CE effect between the liquid and the solid may also make contributions to this process if we select the right materials to trigger the electron transfer on the interface. Moreover, based on DLVO (Derjaguin, Landau, Verwey, Overbeek) theory, the interaction of the electric double layer has a notable influence on the adhesion of colloid particles,¹⁸³ while this adhesion effect can also work for the manipulation of bacterial cells.¹⁸⁴ The charge densities at bacterial cell surfaces depend on the local electric potential (Figure 15d) and this charge density change due to the EDL interaction with another surface, which finally results in the different adhesive behavior of bacterial cells. As described in a previous study,¹⁸⁵ the adsorption flux can be increased with dilute electrolytes due to the EDL interactions among particles. Meanwhile, in the previous study, the calculation for the EDL on the particle-liquid interface considered that the particle surface

has a fixed charge density at the initial state, while there is no indepth discussion about the origin of these initial charges. Then, if we employ the hybrid EDL model in Figure 14, these initial charges may come from the electron transfer process during contact, while calculation of the surface potential may also need to consider the CE effect between the particles and the liquid. A similar situation can also be found in a colloidal suspension,¹⁸⁶ as shown in Figure 15e. In addition, the EDL can function as a nanogap capacitor with huge capacitance, resulting in charge accumulation to a very high level at L-S interfaces, and thus, EDL transistors using ionic liquids or electrolytes as gate dielectrics³⁰ have attracted much attention due to their wide electrochemical windows, low vapor pressures, and high chemical and physical stabilities.¹⁸⁷ EDL transistors can be efficiently gated by a triboelectric potential instead of applying gate voltages (see Figure 15f), which can work as mechanosensitive electronics.¹⁸⁸ Usually ion gels are employed as gate dielectrics and the electrification layer for human-electronics interaction, while the contact electrification on the surface of the ion gel can trigger a voltage signal to control the transistor.¹⁸⁹ In this case, the physical process happening on the surface of the ion gel should be further clarified on the basis of the hybrid EDL model.

7.3. Potential Impact of the Hybrid EDL Model to Other Energy Generators

In addition to the above research fields, some energy harvesters are also related to the EDL. It is well known that a streaming current will be generated when a pressure-driven flow is generated in an aqueous solution in a channel that has a surface charge on its walls.^{190–193} This is because that the EDL will be formed when the aqueous solution is in contact with the charged wall; under external pressure, the ions in the EDL will move directionally, generating a direct current. On the basis of the streaming current, different electric generators were designed for harvesting the energy from ambient environment, as shown in Figure 16a.¹⁹¹ The streaming current can also be generated by dragging a liquid droplet on the graphene surface, as shown in

Figure 16b,^{145,194} and even be generated at the liquid–liquid interface.¹⁹⁵ In order to improve the efficiency of the energy harvester, the effects of different factors, such as the thickness of the EDL, flow velocity, concentration, etc., were discussed,¹ while the identity of the charges, which is one of the key problems in the theory of a hybrid EDL, on the surface of the walls has so far attracted little attention. According to different charge transfer theories (electron transfer or ion transfer), there will be different material selection principles for the streaming current generators. Also, by changing the ions to electrons ratio, the temperature stability of the generators may be improved, since the electrons are more easily excited compared to ions. However, these have not been discussed in the studies of streaming current generators yet. In addition to the streaming current generator, a variety of techniques based on charge transfer at the liquid-solid interface have been invented, such as an electrokinetic energy device,^{196,197} a fiber-shaped fluidic nanogenerator (FFNG),¹⁹⁸ a carbon–water device,¹⁹⁹ etc. In addition, energy harvesting from evaporation has also received attention recently (Figure 16c).²⁰⁰⁻²⁰³ In these techniques, the liquid remains in contact with the solid surface, which is different from the liquid-solid CE. However, electron transfer at the liquid-solid interface is also necessary for these techniques, and their mechanisms are also related to the EDL. Therefore, the Wang transition model and Wang's hybrid EDL theory may have implications on this technique.

8. CONCLUSION AND PERSPECTIVES

In this review, we have summarized recent studies on the mechanisms and applications of liquid—solid CE. Though the charge transfer at the liquid—solid interface is one of the key problems in many fields and the CE has been studied for a long time, the liquid—solid CE has not received much attention. Owing to the invention of liquid—solid TENG, the liquid—solid CE comes to the center stage. The two key problems in liquid—solid CE, the identity of the charge carriers and formation of the EDL, have been systematically studied recently.

In the liquid-solid CE, the solids could be insulators, semiconductors, or metals. For the liquid-insulator CE, we summarized several recent works that demonstrated the existence of electron transfer at the L-S interface using diversified methods both on the microscale and on a large scale. In some cases, the electron transfer even plays a dominant role. The mechanism of the liquid-semiconductor CE is very different from that of the liquid-insulator CE. In the liquidsemiconductor CE, the electron-hole pairs are first excited by the energy released due to the formation of bonds at the interface, which is called "bindington". Then, the electron-hole pairs are separated and directionally move from one surface to the other surface under the driving force of the built-in electric field at the interface, generating a direct tribo-current. This process is similar to the photovoltaic effect, so that it was called the tribovoltaic effect. It is verified that the tribovoltaic effect also exists at the liquid-metal interface, in which the liquid, usually an aqueous solution, is considered as the semiconductor. Regardless of whether the solid side is an insulator, a semiconductor, or a metal, electron transfer plays an important role.

A newly proposed Wang transition model was also introduced in this review. In the Wang transition model, the two atoms are close to each other and the electron clouds belonging to the two atoms overlap with each other, reducing the potential barriers and resulting in electron transfer. When they separate, the electrons belonging to one atom are left on the other atom and the CE occurs.

In addition to the mechanism of the liquid-solid CE, recent progress in the liquid-solid TENG and other applications related to this CE effect were also reviewed. Recently, different liquid-solid TENGs have been designed to harvest the energy from a large surface or designed as a portable and wearable energy package for electronics applications or even combined with another energy technique to establish a hybrid energy generator. We have summarized several key points for designing L-S TENG, including its operation mechanism and the methods of surface treatment. In addition to energy harvesting, CE on the L–S interface can also be applied for sensors, reactors, manipulators, and many ocean-related devices. Furthermore, the L-S TENG can be a probe to determine the electrification at the liquid-solid interface. With further exploration of the fundamental physics of L-S electrification, a series of impacts in related fields is expected in the future.

On the basis of the electron transfer, Wang et al. proposed a hybrid EDL model and a "two-step" formation process, while we provide an in-depth explanation of this concept in this review. In Wang's hybrid EDL model, the electron transfer due to overlap of the electron clouds occurs in the first step. Further, the liquid molecules are pushed away from the solid surface, while the electrons remain. In the second step, free counterions in the liquid are attracted, forming an EDL. A key difference between the hybrid EDL theory and the traditional EDL theory is the identity of the charge carriers in the charged solid surface. The hybrid EDL model considers the electron transfer, while the traditional EDL model does not. The electron and ion are very different; for example, they are different in size, mass, mobility, and diffusion range, and they need a different energy to leave the surface. More importantly, the dynamics related to electrons and ions are very different because electrons can be easily excited by raising the temperature and/or photon excitation, so they are easily leaked out from surfaces/interfaces, which may affect the charge storage capability. Thus far, EDL-related fields, such as electrochemical storage, mechanochemistry, electrocatalysis, electrophoresis, etc., have been based on the traditional EDL model, which may lead to unexplained phenomena. This means that the hybrid EDL model may have significant implications on EDL-related fields, which still remains to be further developed experimentally.

This review focused on introducing studies on liquid–solid CE. In fact, the liquid molecules will collide with each other at the liquid–liquid interface and result in electron transfer as well. Therefore, the concepts and models introduced here for liquid–solid CE, such as the Wang transition model and Wang's hybrid EDL model, may also be suitable for liquid–liquid CE, which has attracted increasing attention. Experimental verification of the correctness of these models in liquid–liquid CE will be one of the key points in the future studies on the CE. Recent study of the contact electrification between water and oil droplet shows that electrons transfer is most likely to dominant charge transfer process.²⁰⁴ A recent review on fundamental theory of contact electrification and TENG can be found at ref 205.

AUTHOR INFORMATION

Corresponding Author

 Zhong Lin Wang – Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, P.
 R. China; School of Materials Science and Engineering,

R

pubs.acs.org/CR

Georgia Institute of Technology, Atlanta, Georgia 30332–0245, United States; • orcid.org/0000-0002-5530-0380; Email: zlwang@gatech.edu

Authors

- Shiquan Lin Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, P.
 R. China; School of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 100049, P. R. China
- Xiangyu Chen Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, P.
 R. China; School of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 100049, P. R. China;
 orcid.org/0000-0002-0711-0275

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemrev.1c00176

Author Contributions

[§]S.L. and X.C.: These authors contributed equally to this review, and the order was decided by a coin toss.

Notes

The authors declare no competing financial interest.

Biographies

Shiquan Lin received his Ph.D. degree from Tsinghua University (THU) in 2018. Since 2018, he has worked as a postdoctoral fellow under the supervision of Prof. Zhong Lin Wang at the Beijing Institute of Nanoenergy and Nanosystems (BINN), Chinese Academy of Sciences. He is now an associate professor at BINN. His research interests include fundamental tribological phenomena, tribovoltaic effect, contact electrification, scanning probe microscopy, and fist-principles calculations.

Xiangyu Chen received his B.S. degree in Electrical Engineering from Tsinghua University in 2007 and his Ph.D. in Electronics Physics from the Tokyo Institute of Technology in 2013. Now he is a professor at the Beijing Institute of Nanoenergy and Nanosystems, Chinese Academic of Sciences. His main research interests are focused on the field of functional dielectric materials, self-powered nanoenergy systems, and a nonlinear optical laser system for characterizing the electrical properties of the devices.

Zhong Lin Wang received his Ph.D. degree from Arizona State University in Physics. He is the Director of the Beijing Institute of Nanoenergy and Nanosystems and Regents' Professor and Hightower Chair at the Georgia Institute of Technology. He pioneered the nanogenerators field for distributed energy, self-powered sensors, and large-scale blue energy. He coined the fields of piezotronics and piezo-phototronics for third-generation semiconductors. Among 100 000 scientists across all fields worldwide, he is ranked #5 in career scientific impact, #1 in Nanoscience, and #2 in Materials Science. His Google scholar citation is over 280 000 with an h index of over 260.

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