CHAPTER

Anticorrosion by triboelectric cathodic protection

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25.1 Introduction

Metal corrosion protection has always been the focus of scientific research and practical application because it will lead to huge economic losses and serious accidents. For example, organic protective coatings and impressed current cathodic protection (ICCP) are widely used to protect buried pipelines or offshore structures. When the organic coating is damaged, ICCP will continue to prevent metal corrosion and keep the metal at a potential more negative than the self-corrosion potential. ICCP requires an external power supply to maintain the persistence of the electron consumption process and lead to the cathodic polarization of the metal. This can lead to problems with fixed power supplies, external power losses, and high maintenance costs. Generally, the power supply system of ICCP usually corresponds to a stable direct current (DC) voltage source or battery, which involves specific restrictions in the use, such as power supply system dependence, periodic replacement, and sustainability. For example, in the case of solar cells, it cannot power the ICCP system at night or in rainy days. In order to solve the above problems and the increasingly serious energy and environmental crisis, it is very important to develop a new intelligent ICCP system with sustainable self-powered supply way. Recently, a new type of energy collection device called triboelectric nanogenerator (TENG) has attracted more and more attention because it directly converts almost all types of mechanical energy existing in our daily life and nature, such as human motion, vibration energy, and wave energy, and converts it into electric energy based on the coupling effect of friction electrification and electrostatic induction.

25.2 Anticorrosion by triboelectric cathodic protection

The static charge generated by the friction electrification process has existed for thousands of years. It has been considered as a negative effect because it is easy to attract dust, cause discharge, and short circuit. Therefore, in most cases, the static charge generated by friction is a waste of electric energy, Pro. Wang and his team [1] invented TENG technology on the basis of friction electrification and electrostatic induction coupling for the first time. It can collect various forms of mechanical energy to convert it into electric energy, such as wind energy, ocean energy, vibration energy,

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and human motion energy. Compared with traditional electromagnetic induction power generation technology, TENG with high power generation voltage, light weight, small volume, flexibility, flexible shape, and high compatibility have attracted extensive attention of researchers. Friction electrification effect is an electron transfer phenomenon caused by the contact of two materials with opposite polarity or relatively different electronegativity. In the process of friction between one material and another material, the atoms on the surface of high electronegativity material will seize electrons from the surface of low electronegativity material due to different electronegativity and take negative charge, while the other material surface takes positive charge [2–7]. The type of charge generated during friction is determined by the relative polarity between the two materials in contact. Wang and Wang [8] explored the mechanism of friction electrification: under the action of mechanical force/pressure, the electron transfer caused by the overlap of electron clouds is the main reason of contact electrification among solid, liquid, and gas.

The advantage of TENG is that it can collect kinds of mechanical energy in life to convert it into electric energy, so it has broad application prospects in production and life. Compared with traditional electromagnetic induction power generation, TENG has various forms of energy collection, high output voltage, and can form a high-strength electric field. At present, the traditional electromagnetic induction generator has many challenges in collecting marine energy, such as it is difficult to collect the mechanical energy generated by waves below 3 Hz. Therefore the simple, reliable, and low-cost TENG provides a new way of large-scale marine energy collection. Lin et al. [9] uses the contact separation between polydimethylsiloxane (PDMS) and water to generate electric energy. Under the control of the motor, PDMS will contact and separate with water body at a constant frequency of 2 Hz, and the voltage of open circuit and alternating current (AC) of TENG can be increased from 0 to 82 V and 33 μA. This work proves for the first time that TENG combined with water can collect the mechanical energy of water wave motion. In nature, the direction and frequency of most mechanical energy is not fixed, so it is difficult to collect energy effectively. Yang et al. [10] proposed a three-dimensional TENG, which can work in both vertical contact separation mode and horizontal sliding mode. As an important mechanical energy given by nature, wind energy is widely regarded as an important renewable green energy. Wind driven friction electrification can convert wind energy into electric energy under weak wind speed, which is of great necessity and practical significance for the development of new wind power generation technology (Fig. 25.1).

This process puts forward higher requirements for the stability of TENG's continuous work. TENG is required to continuously provide energy to achieve efficient cathodic protection (CP), and it is required to have a simpler and more efficient energy conversion mode.

Li et al. [11] uses a network of supercapacitors and TENG to collect a large amount of water energy to prevent metal corrosion. When TENG is integrated with supercapacitors, the output current is stable and continuous. The corrosion results show that TENG-SC self-power supply system can prevent about 80% corrosion of Q235 steel in 0.5 M NaCl solution.

In order to enhance the triboelectric output, the performance of TENG can be enhanced by injecting charge, and a self-powered anticorrosion system can be formed to protect iron from corrosion [12]. Nanostructures are prepared by a simple method and preinjecting charge into the space between the surface of the friction layer and the electrode, so as to greatly improve the performance of the TENG. Due to the nanostructure, the charge density increased by 48%, and further increased by 53% due to the previous charge injection process. The output open circuit voltage reaches

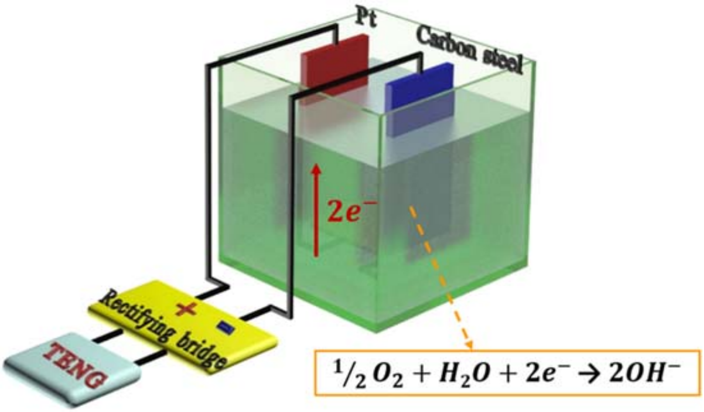

FIGURE 25.1

The scheme of triboelectric cathodic protection.

1008 V. The short-circuit current density reaches 32.1 mA/m^2, and the charge density reaches 121 μC/m^2. This high-performance TENG successfully protects the iron sheet immersed in salt water from corrosion.

Cui et al. [13] prepared a new TENG electrode by electrochemical polymerization with conductive polymer polypyrrole nanowire (PPy NW) as electrode and anodic aluminum oxide as template. TENG based on PPy NW shows high output performance, the maximum short-circuit current density is 23.4 mA m^2, the output voltage is 351 V, and 372 commercial red light emitting diodes (LEDs) can be lit. In addition, a self-powered anticorrosion system powered by TENG based on PPy NW is designed. The system can provide additional electron injection into the surface of the protected metal and form effective ICCP by collecting mechanical energy or wind energy.

Feng et al. [14] prepared a new type of TENG with papers. To further improve the power generation of paper-based TEBF, polydopamine molecules were introduced through simple self-polymerization at room temperature to improve the surface polarity of the friction layer. After chemical modification, the short-circuit current and output voltage are increased by more than 3.5 times, and the maximum values are 30 mA and 1000 V, respectively. The charge density increases from 21 to 76 mC m^2, which can light 496 commercial LEDs. On the basis of this, a set of self-powered CP anticorrosion system is designed to protect A3 steel from corrosion in 3.5% NaCl solution. In addition, the CP system powered by TENG also has good antifouling performance, which can prevent algae from adhering to the metal substrate. This work shows a recyclable, cost-effective paper-based TENG, which has great practical application potential in marine anticorrosion and antifouling.

In terms of wave energy collection, Zhao et al. [15] reported a flexible film TENG for collecting water flow energy. It is the frictional charge at the solid–liquid interface that induces electron flow in the external circuit. By using a surface mounted bridge rectifier array, an area scalable integration method is developed, which ensures a constructive increase in the output current of all electrodes to form pulsed DC. In addition, the surface modification of spin coated nanoparticles can be realized in a large area. Therefore TF-TENG has the potential to expand its scale in the region. The generated electric energy can not only drive small electronic equipment but also effectively ICCP for carbon steel. Therefore TF-TENG is a potential practical solution for on-site continuous power supply, especially for corrosion protection of coastal or offshore sites, as long as wave energy is available.

A self-powered CP system for metal surface protection is designed by using the energy collected from natural raindrops and wind [16]. TENG power supply system can provide a practical energy source for continuously driving CP process without using external power supply. The feasibility of self-powered CP process is verified by stereo microscope, AC impedance measurement, polarization test, and surface tension test. The flexible TENG can produce an efficient CP system for almost all metal structures. It is a very simple manufacturing, high-performance, and cost-effective method to protect metal surfaces from corrosion.

Zhang et al. [17] shows a flexible hybrid nanogenerator (NG), which can collect environmental thermal energy and mechanical energy simultaneously or separately, and can be used in self-powered CP system without using external power supply. Because polyvinylidene fluoride (PVDF) film has the pyroelectric and piezoelectric properties, a polarized PVDF film—based NG is constructed to remove thermal and mechanical energy. The output power of the prepared mixed NG can be directly used to protect the metal surface from chemical corrosion.

Due to the surface nanostructure and other reasons, the preparation process of the above TENG is complex and is not easy to be prepared in a large area. To simplify the preparation method of TENG and facilitate its large-scale use, Wang has developed a series of coating-based TENG (Fig. 25.2).

Microarc oxidation (MAO) and fluorinated sol—gel (FSG) composite coating was prepared [18]. The self-repairing hydrophobic organic/inorganic hybrid coating was used as the friction electric layer. The current output of MAO/FSG composite coating TENG (MF-TENG) is 31 μA. The voltage output is 870 V, 8 times that of MAO-based TENG. Compared with organic coatings, organic/inorganic hybrid coatings have good wear resistance. When the fluorine component on the coating surface is damaged, the self-healing hydrophobicity and electrical output are realized by transferring the loaded perfluorosilane to the damaged surface. The FSG coating has hydrophobicity to ensure that the coating has good corrosion resistance.

Polyacrylic acid (PAA) coating is usually used on the surface of ship equipment with antiaging and antiwear properties. However, when used together with TENG, the friction electric output will be restricted. Liu et al. [19] modified the PAA coating with fluorine-containing polyacrylic acid (F-PAA) resin, which increased its triboelectric output by 6 times and improved its corrosion resistance. In addition, the corrosion resistance can be further enhanced through CP by using the electric output generated by the process of water friction electric energy transfer. TENG based on PAA/F-PAA coating is easy to manufacture and can be used as water energy collection and corrosion resistance. It has broad application prospects in river and marine energy collection and corrosion protection.

In addition, the output current can be doubled through the series parallel mode of TENG, so as to meet the needs of metal corrosion protection (Fig. 25.3).

From the new development of TENG in the application research of metal corrosion protection in recent years, it can be found that TENG has a wide range of materials, cheap and simple preparation, excellent working stability and sustainability, and continuously output performance. At the

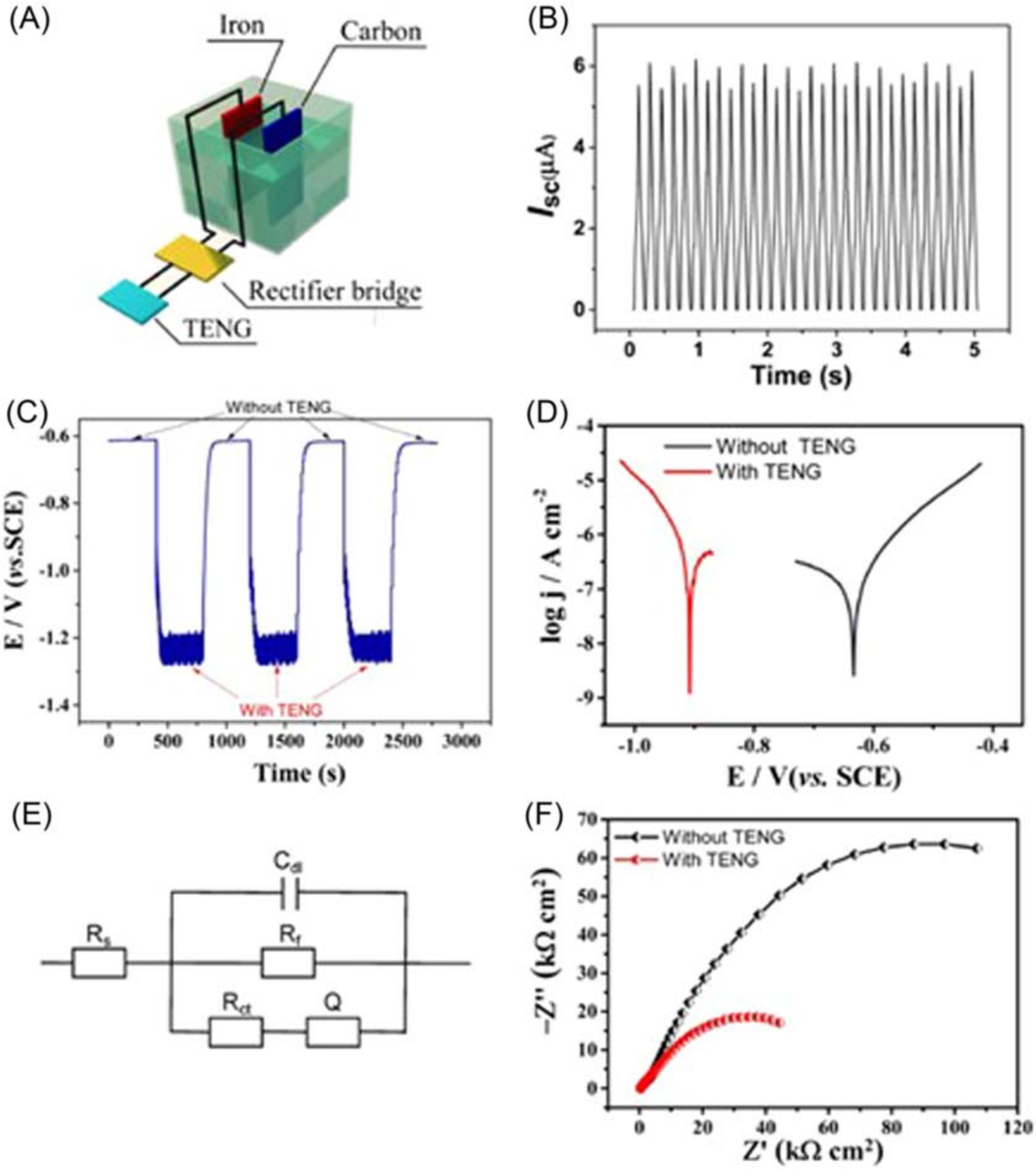

FIGURE 25.2

Anticorrosive protection device powered by FM-TENG. (A) Schematic diagram of anticorrosive protection device powered by FM-TENG. (B) Value of direct current of FM-TENG. (C) Open circuit potential varies of A3 steel supplied with and without FM-TENG. (D) Tafel plots of A3 steel powered with and without FM-TENG. (E) The diagram of equivalent circuit obtained by data fitting. (F) The Nyquist curve of A3 steel with and without anticorrosive protective device.

From C. Xu, Y. Liu, Y. Liu, Y. Zheng, Y. Feng, B. Wang, X. Kong, X. Zhang, D. Wang, New inorganic coating-based triboelectric nanogenerators with anti-wear and self-healing properties for efficient wave energy harvesting, Appl. Mater. Today 20 (2020) 100645. https://doi.org/10.1016/j.apmt.2020.100645.

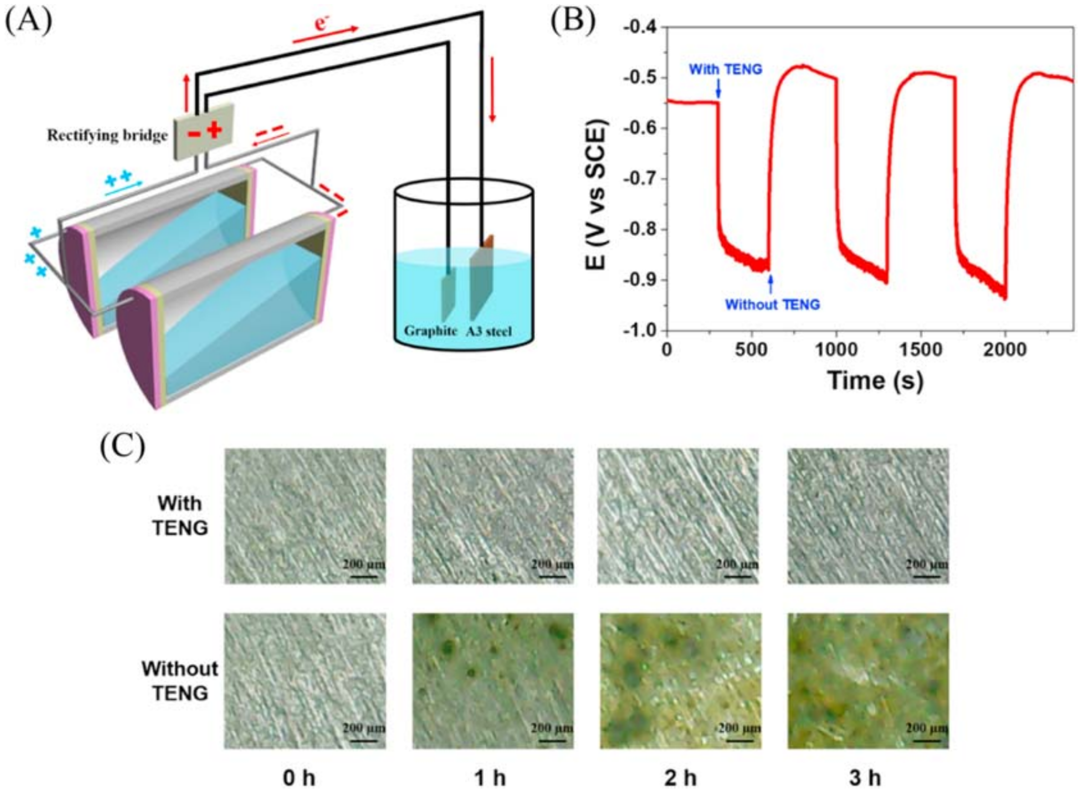

FIGURE 25.3

Device for the solid–liquid TENGs array used for the cathodic protection. (A) Schematic diagram of mechanism and device for the solid–liquid TENGs array used for the cathodic protection of A3 carbon steel in 3.5 wt.% NaCl solution. (B) OCP changes of A3 carbon steel coupled with and without the PTFE-based TENGs. (C) Microscopy images of the A3 carbon steel immersed in 3.5 wt.% NaCl solution for 1, 2, and 3 h, separately, connected with (the top views) and without the PTFE-based TENGs (the bottom views).

From W. Sun, Y. Zheng, T. Li, M. Feng, S. Cui, Y. Liu, S. Chen, D. Wang, Liquid–solid triboelectric nanogenerators array and its applications for wave energy harvesting and self-powered cathodic protection, Energy 217 (2021) 119388. https://doi.org/10.1016/j.energy.2020.119388.

same time, it can also form large-scale integration and be used in combination with external circuit supercapacitors and other devices. It has remarkable protection effect on metal corrosion. Therefore it can be expected that TENG electrochemical CP technology has great development space.

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