Effect of Modified Electrode on Energy Harvesting Based on Contact Electrification

Junmin Lim*, Jeongcheol Shin**,† and Changsuk Yun*,†

*Department of Chemistry, Changwon National University, Changwon 51140, Republic of Korea
**Department of Chemistry, Duksung Women's University, Seoul 01369, Republic of Korea

Abstract

The technology of harvesting energy wasted in daily life is becoming increasingly important for sustainable energy production and climate change. In this study, we investigated an electrochemical energy harvesting system using blue energy generated by the movement of electrodes. We observed that energy could be harvested based on the electrification phenomenon that occurs when an electrode comes into contact with an electrolyte, particularly when the electrode is modified with a self-assembled monolayer (SAM) containing the fluorocarbons. The static charges, which are generated by electrification based on the energy level difference between the electrode and the electrolyte, could be transferred to an external circuit. Additionally, we discovered that structural features of SAM molecules are related to the efficiency of energy harvesting, including the number of fluorocarbons. This system successfully powered an LED, proving the practicality of electrochemical harvesting using blue energy. The results suggest the potential for developing more efficient and high-output energy harvesting systems through the application of various SAM molecules.

Keywords: Self-assembled monolayer, Wasted energy, Energy conversion

1. Introduction

To address the climate crisis, promote sustainable energy production and consumption, and decentralize energy production, various efforts have been made to harvest energy wasted in daily life and convert it into useful forms, such as electrical and chemical energy[1-4]. This conversion process harnesses readily accessible and naturally abundant energy sources including sunlight, wind, waves, and human activities as driving forces[5]. The converted energy can be utilized to operate useful devices such as light-emitting diodes (LEDs), self-powered sensors, and energy storage systems without external power sources[5,6].

Among the diverse naturally abundant energy sources, the large-scale energy associated with the movement of water, such as waves, raindrops, and evaporation, is referred to as blue energy[3,6]. Blue energy, which is easily accessible in the environment, inevitably induces contact between liquids and solids, leading to a physicochemical phenomenon known as contact electrification at the interface between these materials. This process results in charge separation, where one side of the interface becomes positively charged while the other becomes negatively charged. Although the detailed electrification mechanisms are still under debate with numerous hypotheses involving

electrons, ions, and radicals, the excess charge generated on the material's surface is transferred outside, and utilized for practical applications assisted by a device known as an energy harvester[7-11].

Electrochemical systems include liquid electrolytes and solid electrodes, providing a method for energy harvesting from the electrification induced by blue energy. Recent studies have shown that modification of electrodes with self-assembled monolayers (SAMs) can harvest mechanical energy based on the change in contact area at the electrode-electrolyte interface[12]. Therefore, the electrification phenomenon occurs, allowing the resulting static charges to perform work in an external circuit. The degree of electrification depends on the energy level difference between the SAM-modified electrode and the electrolyte, which contains redox pairs. Notably, the electrode's energy level can be readily tuned by the direction and magnitude of the dipole within the SAM molecules on the electrode[13,14]. Therefore, it becomes a critical factor for highly efficient energy harvesting.

In this study, we observed electrochemical energy harvesting based on the electrification phenomenon occurring at modified electrode-electrolyte interface. The influence of electrode modifications on this harvesting was investigated using fluorinated SAMs with different numbers of fluorocarbons, as examined in previous studies[12]. The energy level of this modified electrode does not significantly change compared to previous, because the number of fluorocarbons in the SAM exceeds a certain threshold. The electrification of the interface between the SAM/electrode and the ferricyanide/ferrocyanide electrolyte was reproducible and repetitive, assisted by the mechanical motion of a stepper motor. The electrical signals generated by this process were systematically analyzed using Data Acquisition (DAQ). Our results in-

† Corresponding Author: J. Shin: Duksung Women's University, Department of Chemistry, Seoul 01369, Republic of Korea;
C. Yun: Changwon National University, Department of Chemistry, Changwon 51140, Republic of Korea
Tel: J. Shin: +82-2-901-8353; C. Yun: +82-55-213-3436
e-mail: J. Shin: jcshin91@duksung.ac.kr; C. Yun: csyun@changwon.ac.kr

dicate that even electrodes tuned to similar energy levels can exhibit different energy harvesting/conversion performances, highlighting the significance of other unconsidered factors.

2. Experiment

2.1. Materials

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanethiol (Sigma-Aldrich, 97%), $KClO_4$ (Sigma-Aldrich, 99.0%), potassium hexacyanoferrate(III) (Sigma-Aldrich, 99%), and potassium hexacyanoferrate(II) trihydrate (Sigma-Aldrich, 98.5~102%) were utilized in this study. All electrolytes were prepared with ultrapure water (18.2 MΩ·cm). The 150 nm Au/Si wafer and the 1 mm Au wire (Thermo Scientific, 99.95%, 1 mm diameter) are used as gold electrodes.

2.2. Formation of self-assembled monolayer on the electrode

To form SAM layer on the electrode surface, the electrode was cleaned in piranha solution (sulfuric acid: hydrogen peroxide, 3:1 v/v) for 3 minutes. The clean Au electrodes were stored in a SAM/EtOH solution (1:1000, v/v) maintained at 42°C for over 16 hours. To confirm the successful formation of SAM on the electrode, cyclic voltammetry (CV) experiment was performed using a potentiostat (CH Instruments, CHI 650) with a three-electrode system. The Au wafer, Pt wire, and Ag/AgCl electrodes (3 M KCl) were used as the working electrode, counter electrode, and reference electrode, respectively. 0.1 M $KClO_4$ solution was utilized as the supporting electrolyte, and a mixture solution of 1 mM ferricyanide and 1 mM ferrocyanide was used as the redox couple.

2.3. Energy harvesting at the modified electrode/electrolyte interface based on electrification

To induce electrification between the SAM-modified electrode and the electrolyte, a two-electrode system was used, consisting of a SAM/Au electrode and a bare Au electrode. The SAM/Au wire connected to the positive terminal was fixed on the *z*-axis of a stepper motor and moved in the ferricyanide/ferrocyanide solution with 0.1 M $KClO_4$ solution at specific speeds and displacements (10, 20, 30, 40 mm/s, 13 mm) at 10-second intervals. The bare Au electrode connected to the negative terminal remained stationary. The voltage generated by the mechanical movement of the SAM/Au electrode was measured in parallel using DAQ (National Instruments, USB- 6002) with a recording interval every 1000 kHz. To verify whether the charged energy could be transmitted to an external circuit, a 100 kΩ resistor was connected in parallel in the same setup.

2.4. Energy harvesting using LED

The energy conversion was visually observed using a red LED with a forward voltage of approximately 1.4 V instead of a resistor. A 1.2 V nickel-metal hydride battery was included in the circuit to compensate for the insufficient output of the system. The SAM/Au electrode moved periodically along the *z*-axis of the stepper motor at 10-second intervals. The switching on and off of the LED in response to the me-
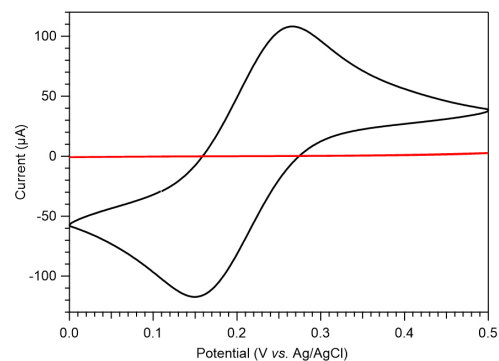

Figure 1. Cyclic voltammetry of bare Au wafer (black) and SAM/Au wafer (red) in 1 mM ferricyanide and 1 mM ferrocyanide solution containing 0.1 M $KClO_4$ solution. Scan rate: 25 mV/s.

chanical movement of the electrode was recorded using a camera equipped in smartphone (SAMSUNG, GALAXY NOTE 20 ULTRA).

3. Results and discussion

The interface between the electrolyte and the Au electrode must be sufficiently slippery for smooth electrification to occur. Additionally, electrode modification is necessary to tune the energy level of bare Au and ensure that the excess charge generated is transmitted to an external circuit before dissipation. Therefore, a hydrophobic SAM molecule was used to form a dielectric layer on the hydrophilic Au electrode surface. A SAM molecule containing six fluorocarbons was used for the modification of the electrode, and a blocking effect for the typical redox reaction was observed due to the well-ordered SAMs on the gold surface (Figure 1). The Au electrode modified with SAM exhibited a significantly lower electrochemical current and no peak current compared to the bare electrode.

Figure 2(a) illustrates the process of electrification between a SAM/Au electrode and an electrolyte, as well as the measurement of the resulting electrical signals. The SAM/Au electrode, connected to the positive terminal of the DAQ, moves periodically using a stepper motor, while the counter bare Au electrode, connected to the negative terminal, remains stationary. Figure 2(b) shows the voltage generated by the same mechanical motion for both the SAM/Au and bare Au electrodes, revealing different trends. Although both electrodes displayed an offset value close to 0 V in the null system, the voltage of the SAM/Au electrode increased during the immersion step, whereas the bare Au electrode exhibited no signal. Similarly, during the withdrawal process, the voltage of the SAM/Au electrode increased in the opposite direction, whereas the bare Au electrode showed no change. These results indicate that the functionality of the SAM coating on the electrode surface is essential for electrification. Firstly, the hydrophobic SAM molecule induces appropriate changes in the contact area without interacting with the electrolyte during mechanical motion. Secondly, the dipole of the SAM molecule tunes the energy level of the electrode, causing the energy difference with the electrolyte to increase, leading to electrification. Thirdly, the SAM molecule acts as a dielec-
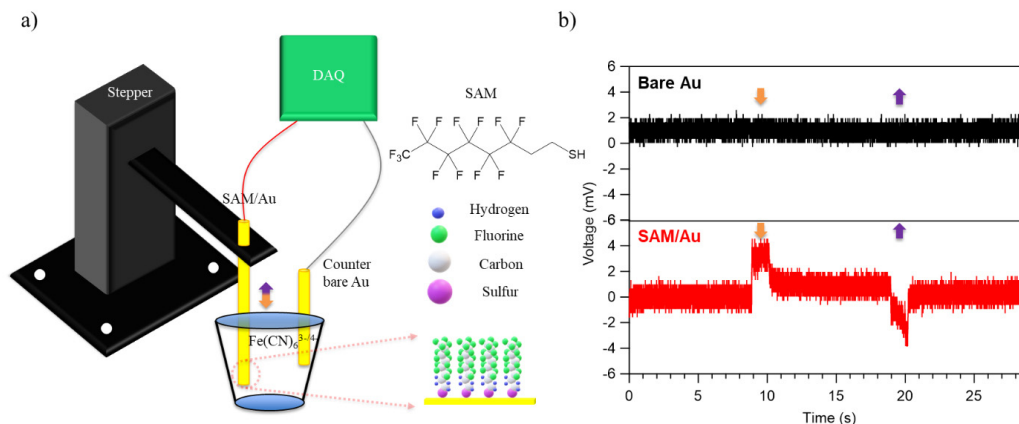
a)

b)

Figure 2. (a) Scheme for measurement of voltage generated by Au wires based on difference between the work function of the modified metal and the chemical potential of the redox electrolyte. **(b)** Voltage generated by moving of bare Au wire (black) and SAM/Au wire (red) in 1 mM ferricyanide and 1 mM ferrocyanide solution containing 0.1 M KClO$_4$ solution. Speed (10 mm/s), displacement (13 mm), and time interval (10 s) of Au moving controlled by *z*-axis stage.
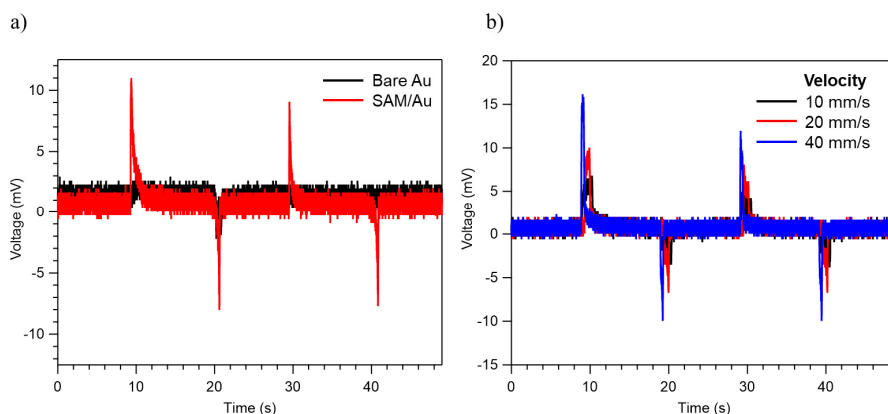
a)

b)

Figure 3. (a) Transmitted energy from the electrode/electrolyte interface to a 100 kΩ resistor when moving the bare Au wire (black) and SAM/Au wire (red) in 1 mM ferricyanide and 1 mM ferrocyanide solution containing 0.1 M KClO$_4$ solution. **(b)** Velocity dependence of transmitted energy from the electrode/electrolyte interface to a 100 kΩ resistor in the same solution. Speeds: 10 mm/s, 20 mm/s, 40 mm/s; displacement: 13 mm; time interval: 10 s, controlled by *z*-axis stage.

tric layer on the electrode surface, prolonging the discharge time of the charged interface to the order of seconds, allowing for transmission to an external circuit.

We recognized that voltage was generated when the contact area between the SAM-modified Au electrode and the electrolyte changed, as shown in Figure 2. A 100 kΩ resistor was used to investigate whether the excess charge generated at the electrode interface could be transmitted to an external circuit. The voltage across the resistor is directly related to the extent of charge transfer from the charged electrode surface to the external circuit. The speed and displacement of the stepper motor and the chemical composition of the electrolyte were kept constant as in Figure 2, except for the parallel connection of the resistor.

In Figure 3(a), voltage was generated by mechanical movement even with the resistor in place. The calculated power was approximately 1 nW, which is an order of magnitude lower than that of a SAM containing eight fluorocarbons. This result suggests that in addition to the relative energy difference between the modified electrode and the elec-

trolyte, other physicochemical factors may also influence electrochemical energy conversion. There may be at least two components to consider. (1) The stability of SAM layer depends on interchain interactions related to the chain length of SAM molecules[15]. (2) The degree of wetting may change due to hydrogen bonding or dipole-dipole interactions between the fluorocarbons in the chain and the electrolyte[14,16]. This implies that even minor differences in the structure of SAM molecules can significantly affect the performance. In contrast, the bare Au electrode did not generate any voltage although the same mechanical motion was applied. Figure 3(b) shows the velocity dependence of the generated voltage. The peak voltage occurs more quickly at higher speeds, and the peak voltage also increases with the speed of the SAM/Au electrode movement. This characteristic implies that the output can be adjusted to operate specific devices.

Mechanical energy generated by the movement of the SAM/Au electrode could be converted into electrical energy based on the electrification phenomenon in an electrochemical system. Figure 4 shows
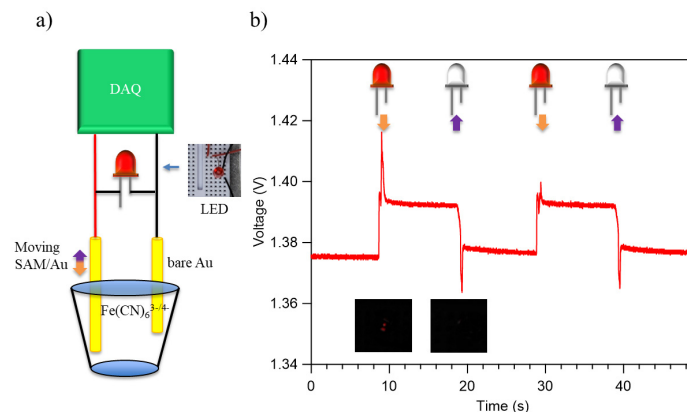
Figure 4. (a) Scheme for energy harvesting based on the periodic movement of SAM/Au in 1 mM ferricyanide and 1 mM ferrocyanide solutions containing 0.1 M KClO₄ solution. (b) The red LED turns on or off depending on the moving direction of the SAM/Au electrode in the electrolyte. Transmitted energy from the electrode/electrolyte interface to the LED. Speed: 40 mm/s, displacement: 25 mm, and time interval: 10 s, controlled by the *z*-axis stage.

a demonstration of an energy harvester that could be utilized in daily life by connecting a red LED to the same setup. The velocity dependence observed in Figure 3(b) should be considered to obtain sufficient output to switch on the LED. The SAM/Au electrode immersed in the electrolyte was periodically moved at a maximum speed of 40 mm/s, which is the maximum speed allowed by the stepper motor. Figure 4(b) presents the signal in response to mechanical movement, similar to the results in Figure 2, where the voltage momentarily increased in the positive direction during the immersion step. When the voltage exceeded the forward voltage, the red LED lit up temporarily. These results indicate that energy harvesting based on an electrochemical system is feasible, provided the electrode is modified with SAM molecules possessing appropriate physicochemical properties. Therefore, further research using various SAM molecules could lead to the development of a more efficient and higher-output energy harvesting system.

4. Conclusion

In this study, we investigated an electrochemical energy harvesting system that utilizes blue energy, by employing electrodes modified with SAMs. The results demonstrated that the structural parameter of the SAM molecules on the electrode surface, particularly the number of fluorocarbons, significantly influences the electrode-electrolyte interaction and the energy conversion efficiency. The SAM-modified electrodes were electrified by changing the contact area with the electrolyte based on mechanical motion, and the generated charges were successfully transmitted to an external circuit, allowing for effective energy harvesting. Additionally, this system could power an LED, demonstrating the practical potential of blue energy harvesting. This study suggests the possibility of developing more efficient and high-output energy harvesting systems through the application of various SAM molecules, contributing to sustainable energy production.

References

1. D. Andrew, R. Mallick, H. A. García, and P. Keikhaei Dehdez, Energy harvesting from pavements. In: K. Gopalakrishnan, W. J. Steyn, and J. Harvey (eds.). *Climate Change, Energy, Sustainability and Pavements*, 481-505, Springer, Berlin/Heidelberg, Germany (2014).

2. V. Pecunia, S. R. Silva, J. Phillips, E. Artegiani, A. Romeo, H. Shim, J. Park, J. Kim, J. S. Yun, G. Welch, B. Larson, M. Creran, A. Laventure, K. Sasitharan, N. Flores-Diaz, M. Freitag, J. Xu, T. Brown, B. Li, and A. Joshi, Roadmap on energy harvesting materials, *J. Phys. Mater.*, **6**, 042501 (2023).

3. G. Liu, T. Chen, J. Xu, and K. Wang, Blue energy harvesting on nanostructured carbon materials, *J. Mater. Chem. A*, **6**, 18357-18377 (2018).

4. A. Berbille, X. Li, Y. Su, S. Li, X. Zhao, L. Zhu, and Z. L. Wang, Mechanism for generating H₂O₂ at water-solid interface by contact-electrification, *Adv. Mater.*, **35**, 2304387 (2023).

5. W. Kim, D. Kim, I. Tcho, J. Kim, M. Kim, and Y. Choi, Triboelectric nanogenerator: Structure, mechanism, and applications, *ACS Nano*, **15**, 258-287 (2021).

6. T. Zhao, M. Xu, X. Xiao, Y. Ma, Z. Li, and Z. L. Wang, Recent progress in blue energy harvesting for powering distributed sensors in ocean, *Nano Energy*, **88**, 106199 (2021).

7. B. Baytekin, H. T. Baytekin, and B. A. Grzybowski, What really drives chemical reactions on contact charged surfaces?, *J. Am. Chem. Soc.*, **134**, 7223-7226 (2012).

8. H. T. Baytekin, B. Baytekin, S. Huda, Z. Yavuz, and B. A. Grzybowski, Mechanochemical activation and patterning of an adhesive surface toward nanoparticle deposition, *J. Am. Chem. Soc.*, **137**, 1726-1729 (2015).

9. C. Yun, S. Lee, J. Ryu, K. Park, J. Jang, J. Kwak, and S. Hwang,

Can static electricity on a conductor drive a redox reaction: Contact electrification of au by polydimethylsiloxane, charge inversion in water, and redox reaction, *J. Am. Chem. Soc.*, **140**, 14687-14695 (2018).

10. H. Qin, L. Xu, F. Zhan, and Z. L. Wang, Electron transfer induced contact-electrification at oil and oleophobic dielectric interface, *Nano Energy*, **116**, 108762 (2023).

11. S. Lin, X. Chen, and Z. L. Wang, Contact electrification at the liquid-solid interface, *Chem. Rev.*, **122**, 5209-5232 (2022).

12. C. Yun, T. D. Dinh, and S. Hwang, Chemical electrification at solid/liquid/air interface by surface dipole of self-assembled monolayer and harvesting energy of moving water, *J. Colloid Interface Sci.*, **615**, 59-68 (2022).

13. J. S. Eo, J. Shin, S. Yang, T. Jeon, J. Lee, S. Choi, C. Lee, and G. Wang, Tailoring the interfacial band offset by the molecular dipole orientation for a molecular heterojunction selector, *Adv. Sci.*, **8**, 2101390 (2021).

14. H. J. Lee, A. C. Jamison, and T. R. Lee, Surface dipoles: A growing body of evidence supports their impact and importance, *Acc. Chem. Res.*, **48**, 3007-3015 (2015).

15. A. Truyens, J. Vekeman, and F. Tielens, A subtle balance between in- terchain interactions and surface reconstruction at the origin of the alkylthiol/Au(111) self-assembled monolayer geometry, *Surf. Sci.*, **696**, 121597 (2020).

16. D. Barriet and T. R. Lee, Fluorinated self-assembled monolayers: composition, structure and interfacial properties, *Curr. Opin. Colloid Interface Sci.*, **8**, 236-242 (2003).

Authors

Junmin Lim; B.Sc., Student, Department of Chemistry, Changwon National University, Changwon 51140, Republic of Korea; dlawn sals846@naver.com

Jeongcheol Shin; Ph.D., Assistant Professor, Department of Chemistry, Duksung Women's University, Seoul 01369, Republic of Korea; jcshin91@duksung.ac.kr

Changsuk Yun; Ph.D., Assistant Professor, Department of Chemistry, Changwon National University, Changwon 51140, Republic of Korea; csyun@changwon.ac.kr