An Ionic Polymer Metal Composite Based Electrochemical Conversion System in the Ocean

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In the ocean, there are a wide variety of offshore plants, and these stand-alone plants require electrical energy. Turbines can be used to convert ocean kinetic energy into electrical energy but these turbines are fixed structures, which are not advantageous. Electro active polymers are playing an important role due to their electricity generation characteristics corresponding to mechanical stimuli. Piezoelectric materials have long been used to turn kinetic energy into electrical energy. Although they have showed remarkable electrical energy generation in several applications, their brittleness and response characteristics only to high frequency stimuli limit their various applications. The use of ionic polymer metal composites can be a solution to overcome the drawbacks of piezoelectric materials since ionic materials are soft and they better respond to the low frequency stimuli. Moreover their intimacy with water enables them to be used in water environment, which is fit for ocean kinetic energy harvesting. However, they show low energy generation density per unit area when compared with other energy sources. In this study, an ocean kinetic energy harvesting module has been constructed and operated with newly developed graphene-based ionic polymer metal composite as an electrochemical material. The module can be relocated to accommodate certain applications to efficiently capture both vertical waves and horizontal ocean currents to supply electricity to stand-alone offshore plants. The module produces electrical energy over the target of 120 Wh and up to 600 Wh for 20 days. Since then, the growth of algae and barnacles on the module retard the electrochemical material's motion and disrupt harvesting of the electrical energy. The ocean kinetic energy harvesting module has the potential to

coexist with marine environments and represent an advance toward the sustainable utilization and development of marine resources.

1. INTRODUCTION

Oceanic energy harvesting has become an important aspect of maritime energy recovery to support mankind. The ocean holds a tremendous amount of untapped energy. Ocean energy technologies are in the early stages of development compared to other renewable technologies. There are only a few tidal barrage installations operating in the world on a commercial basis. Ocean energy technologies can be divided into the following categories: tidal rise and fall, waves, tidal currents, ocean currents, thermal gradients and salinity gradients [1]. First proposed less than 40 years ago, systems to harvest utility-scale electrical power from ocean waves have recently been gaining momentum as a viable technology [2]. Since the early 1980s, a well-understood theory has existed for the optimal absorption of energy by wave energy converter (WEC) arrays of various geometries for waves oscillating at a single frequency [3, 4]. Since early in the twentieth century, it has been well known that without mixing, such a system would stall. The depths would fill with cold water, which is dense, because it would not resurface, leaving a thin warm layer on top. The warmth is needed to add buoyancy to the bottom waters, which requires mixing of the water layers. With so many new results, the researchers who study ocean mixing are scrambling to incorporate them all [5]. The ocean surface boundary layer mediates air-sea exchange. In the classical paradigm and in current climate models, its turbulence is driven by atmospheric forcing [6]. Typically, WECs are nearly invisible from the shore. Wave climates are also more predictable than some other renewable sources including wind. Nonetheless, similar to all renewables, wave energy has a much smaller energy density than fossil fuels and requires a higher capital investment [7]. A wide variety of WECs have been proposed to extract power from the ocean [8]. In comparison to the more familiar surface waves, internal waves are much slower, with periods of hours instead of seconds. Some of the energy lost by breaking internal waves increases the potential energy of the ocean by mixing stratified water and raising its center of mass. It is this potential energy that is eventually converted to the kinetic energy of the meridional overturning circulation [9, 10].

The conversion of the energy in ocean waves into usable electrical power is not trivial. An electrical conversion system is needed between the WEC and the grid [11]. The point absorber and oscillating water column WEC devices address commercial prospects, environmental concerns, current state-of-the art and future research areas [12]. The method of aggregate power smoothing from multiple WECs to improve the power quality will be investigated. Because the incoming wave energy is nearly constant when averaged over longer periods of time, the power production can be equally averaged by covering a large distance of the incoming wave. Substantial work has been performed in this area, and the successful integration of WECs into a farm system has been demonstrated [13-15].

There are a number of different technologies for extracting energy from marine currents including horizontal and vertical-axis turbines as well as venturis and oscillating foils [16]. ISWEC (Inertial Sea Wave Energy Converter) uses a gyroscope to create an internal inertial reaction that is able to harvest wave power without exposing mechanical parts to the harsh oceanic environment. In fact, ISWEC externally appears as a monolithic float. The float rocks in reaction to the incoming wave, and the gyroscopic system is sealed inside. The gyroscope drives a power take-off (PTO) system that converts mechanical power into electrical power [17].

Until now, research on electrochemical WECs has been limited because current methods for IPMC manufacture rely on expensive noble metal platinum complex solution [18]. Therefore, we have developed a highly electrically conductive graphene-based ink solution that is inexpensive and durable in marine environments to replace the platinum electrode layers in IPMC. When the IPMC bends due to kinetic energy, a voltage is generated between the two electrodes across the membrane in both air and water. The instantaneous power density of the state-of-the-art IPMC is approximately 20 W/m^3 with an average efficiency of approximately 2% or less [19]. Inspired by the hydrophilic capability of IPMC, we were challenged to develop a method where sensor-level powered IPMC materials can be scaled-up to a movable power generator.

In this study, a cost effective electrode coating method on the surface of Nafion, an electrolyte polymer membrane utilized in IPMC fabrications, was investigated. The graphene powder and liquid Nafion mixture based conductive ink was developed and directly applied on the surface of large scale Nafion films. The effectiveness of the fabricated membrane as an energy harvester was tested by installing multiple pieces under buoys and measuring the generated power from them oscillating corresponding to the movement of buoys due to kinetic energy of waves. To integrate multiple pieces of films under buoys, we designed an innovative module of which graphite electrodes firmly fixes the film pieces under water. By doing so, a remarkable improvement of energy harvesting ability was observed.

2. EXPERIMENTAL PROCEDURE

We developed an electrochemical material consisting of Nafion film coated with a grapheme based conductive ink to build an ocean kinetic energy harvesting structure to supply electricity to stand-alone offshore plants to accommodate situations that require reduced costs and expanded coverage.

Therefore, we have developed a highly electrically conductive graphene-based ink solution that is inexpensive and durable in marine environments to replace the platinum electrode layers in IPMC. The conversion performances for the conversion from kinetic energy to electrical energy with a wide variety of conductive graphene-based solutions were experimentally investigated in both air and seawater, and the optimal wt% of material content is reported in Table 1. Nafion content in isopropyl alcohol was obtained from DuPont, Inc. The type of conductive particles mixed with the Nafion dispersion are reported in Table 1 and divided into three groups based on their material properties and particle sizes.

Table 1. Raw materials and proportion of the conductive grapheme-based solution.

| Raw material	Proportion (wt%)
Nafion	60.5
Graphene	5
CNT	0.25
Acetylene blackpigment	0.25
Molybdenum	0.5
Nickel	0.5
Polyaniline	0.5
Isopropyl alcohol	25
Butyl cellosolve	7

To enhance the hydrophilic capability of IPMC, we constructed an experimental apparatus in air shown in Fig. 1(a) and an experimental simulator in seawater shown in Fig. 1(b), and then, we tested the performance of the IPMC with a variety of conductive graphene-based solutions in both the air and seawater. The test was conducted by applying the same bending motions to the IPMC samples while the frequencies were varied from 0.03 Hz to 1 Hz. Due to their inherent flexibility, mechanoelectric coupling, ability to operate in both water and air, and long operating life, IPMCs are excellent candidates for harvesting energy in the low frequency regime.
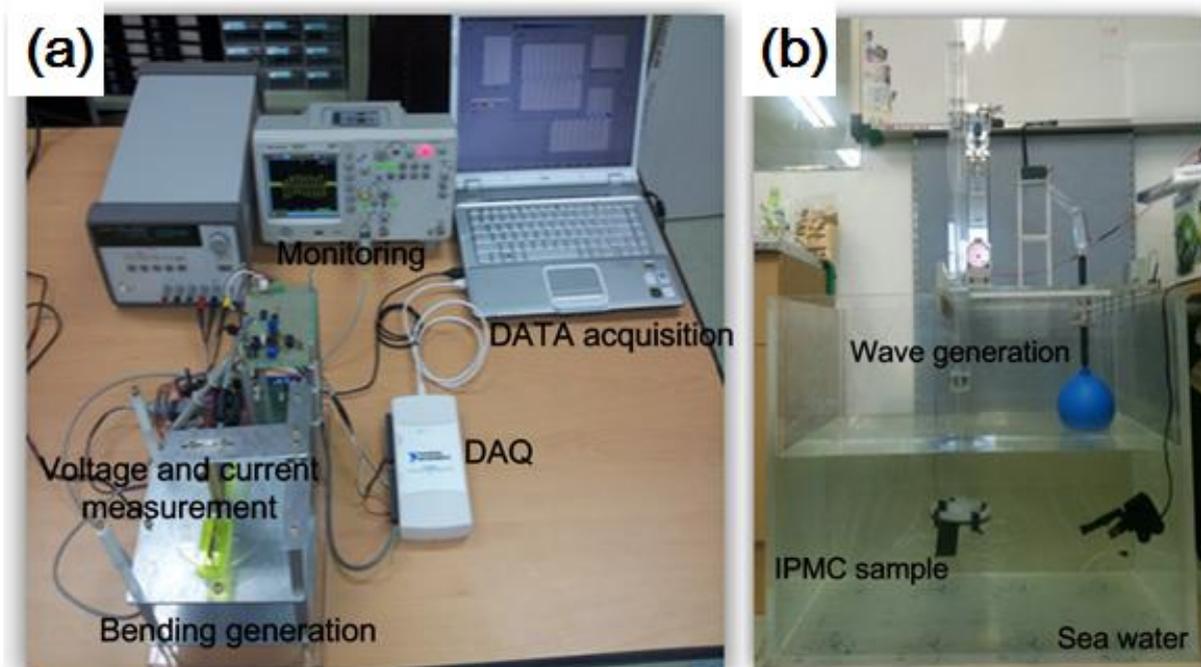
Figure 1. (a) An experimental apparatus in air and (b) an experimental simulator in seawater for evaluating the conversion performance from kinetic energy to electrical energy with graphene-based IPMC and Pt-based IPMC.

The ocean kinetic energy harvesting module consists of nine vertical and nine horizontal components with ten cells. The cell has two upper and lower mold injected plastic square-shaped frames, an IPMC between two graphite electrodes in every face and a circuit for rectifying and parallel collecting electricity. The entire cell is waterproof. Both the vertical and horizontal components have a sub-buoy sufficient to float on the surface of the seawater, and each component composed of ten cells has an electricity collector in parallel located on the sub-buoy. A main buoy, which is composed of eighteen components, consists of an electricity collector in parallel with power measurement and a communication module with a photovoltaic power supply that wirelessly sends data to a monitoring system. Nine vertical and nine horizontal components, which are placed on the left and right sides of the main buoy, respectively, are connected to each other with ropes, and the main buoy is fixed to the seafloor with four anchors.

Based on the results of the IPMC sample performance with the conductive graphene-based solution and the investigation of the marine physics, we optimized the total active area of the ocean kinetic energy harvesting module with IPMC. The performance of the IPMC with the electrical conductive graphene-based solution is slightly worse than that with the platinum complex solution. Therefore, a less than one and half times broader active area was prepared (i.e., 16,200 cm^2), which consists of eighteen for each component containing ten cells with an active area of 900 cm^2.
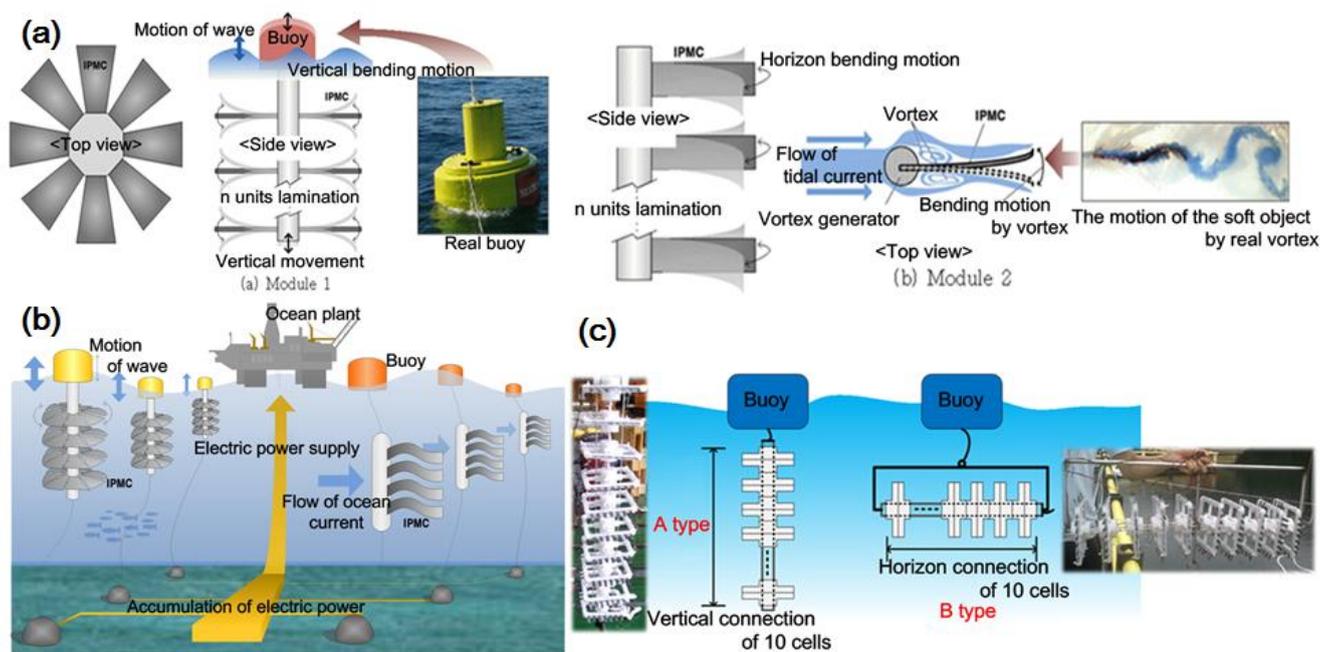
Figure 2. Conceptual designs of the ocean kinetic energy harvesting structure with an electrochemical material consisting of IPMC. (a) Illustration of a compact movable power system utilizing both vertical wave and horizontal ocean current with a vortex. (b) Schematics of ocean kinetic energy harvesting structure with an electrochemical material consisting of IPMC supplying electricity for stand-alone offshore plants. (c) Design and fabrication of a transverse component for the vertical motion of the waves and a longitudinal component for the horizontal motion of the ocean currents.

We designed a movable power system utilizing both vertical waves and horizontal ocean currents using the electrochemical material consisting of IPMC to supply electricity to stand-alone offshore plants, as shown in Figs. 2(a), 2(b) and 2(c). Water movements are a combination of both transverse and longitudinal components. The transverse component accounts for the vertical motion of waves, and the longitudinal component refers to the horizontal motion of ocean currents, as shown in Fig. 2(c) [20-22].

3. RESULTS AND DISCUSSION

3.1 SEM analyses of electrochemical materials

The different sized particles were used to improve the conductivity and abrasion resistivity by filling the spaces between larger particles with the relatively small particles upon mixing. The first group consists of carbon-based particles including graphene and single wall carbon nanotubes obtained from WorldTube, Inc. in South Korea, which have a particle size distribution ranging from 50 to 100 nm. Because the single wall carbon nanotubes (CNTs) exhibit a strong absorption characteristic, only a small portion (i.e., 0.25 wt%) was used. The second group consists of a conductive polymer and a conductive black pigment. 0.5 wt% of the conductive polymer (i.e., polyaniline) and 0.25 wt% of a conductive pigment (i.e., acetylene black), which has needle type crystals that can improve conductivity by connecting to other particles, were used. The mean particle sizes of these materials were 30 nm and 100 nm, respectively. The third group consists of metal-based particles including molybdenum and nickel powders that have relatively large particle sizes, which range from 15 μm to 20 μm, and improve the conductivity of the ink. 25 wt% of isopropyl alcohol was added to improve the adhesion of the ink to the Nafion film and to dissolve the particles. 7 wt% of butyl cellosolve was added to control the volatility of the ink. All of the materials were mixed using high speed dispersion with zirconium beads. After the ink was applied to the surface of the Nafion 117 membrane using an air spray, the membrane was fully dried at 140 °C in oven for 1 hour.

Fig. 3 shows a comparison of the surface (500x) and cross-sectional (5000x) SEM images between graphene-based IPMC and platinum-based IPMC at a magnification enough to differentiate microstructures at the surface of electrode and membrane. Both graphene-based and platinum-based IPMCs are uniformly dispersed at the surface of electrode and the connective layer between electrode and membrane.
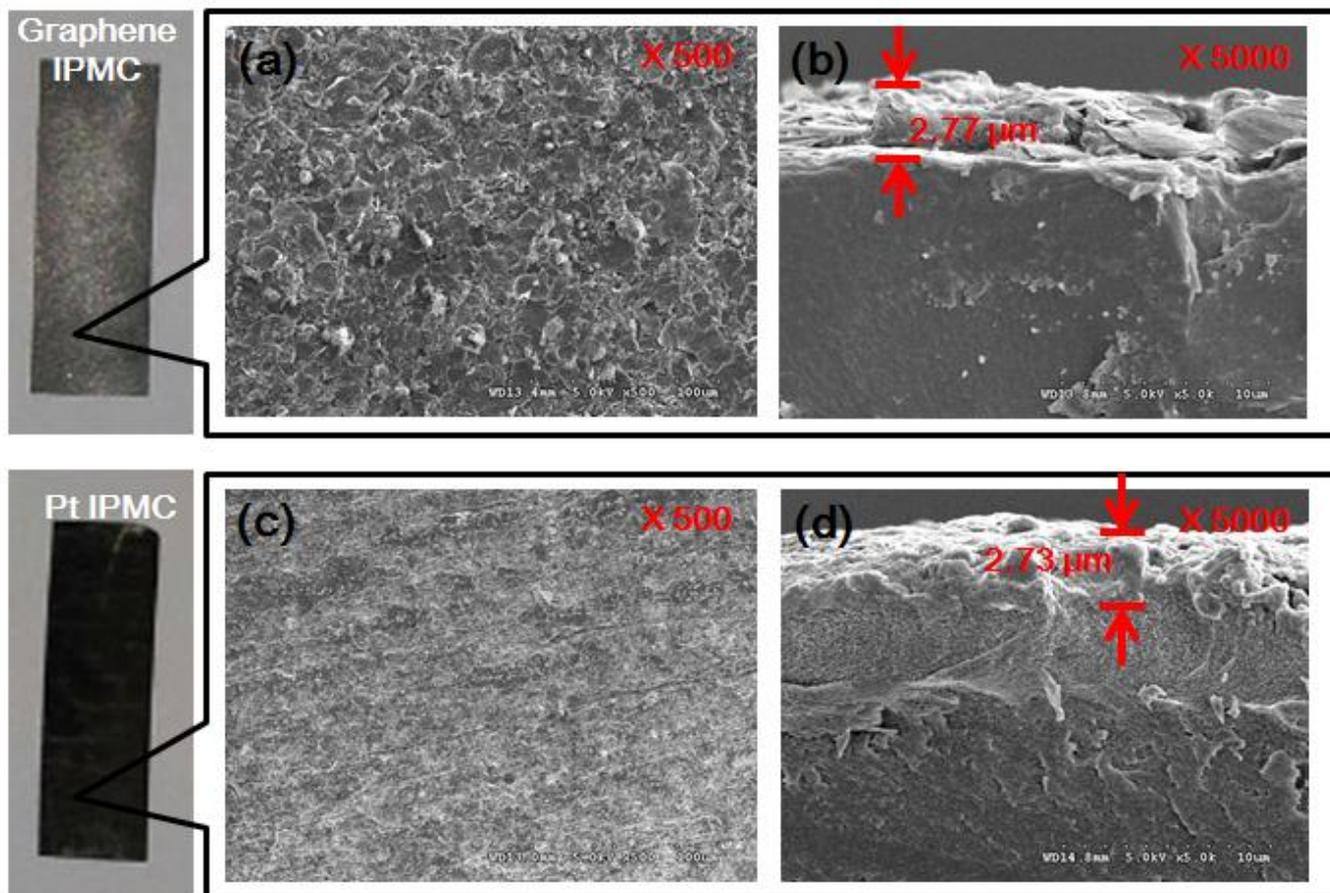
Figure 3. SEM image comparison of graphene based IPMC and platinum based IPMC. (a) Surface SEM image of graphene based IPMC. (b) Cross sectional SEM image of graphene based IPMC. (c) Surface SEM image of platinum based IPMC. (d) Cross sectional SEM image of platinum based IPMC.

3.2 Laboratory scale test for harvesting electrical energy

The test results indicated the performance of the IPMC samples with the conductive graphene-based solution and the platinum complex solution in both air and seawater, as shown in Figs. 4(a) and 4(b) respectively. As the raw materials and mixing ratio were optimized, the voltage in the IPMC sample with the conductive graphene-based ink solution increased. The voltage in the IPMC sample with the conductive graphene-based solution is 58% smaller than that for the IPMC sample with the platinum electrode in air. However, the difference becomes decreased by 18% in seawater due to the hydrophilic properties. In comparison to the IPMC with the platinum complex solution, the IPMC with the graphene-based solution is significantly more efficient at generating larger voltages under application of higher power in the ocean [23].
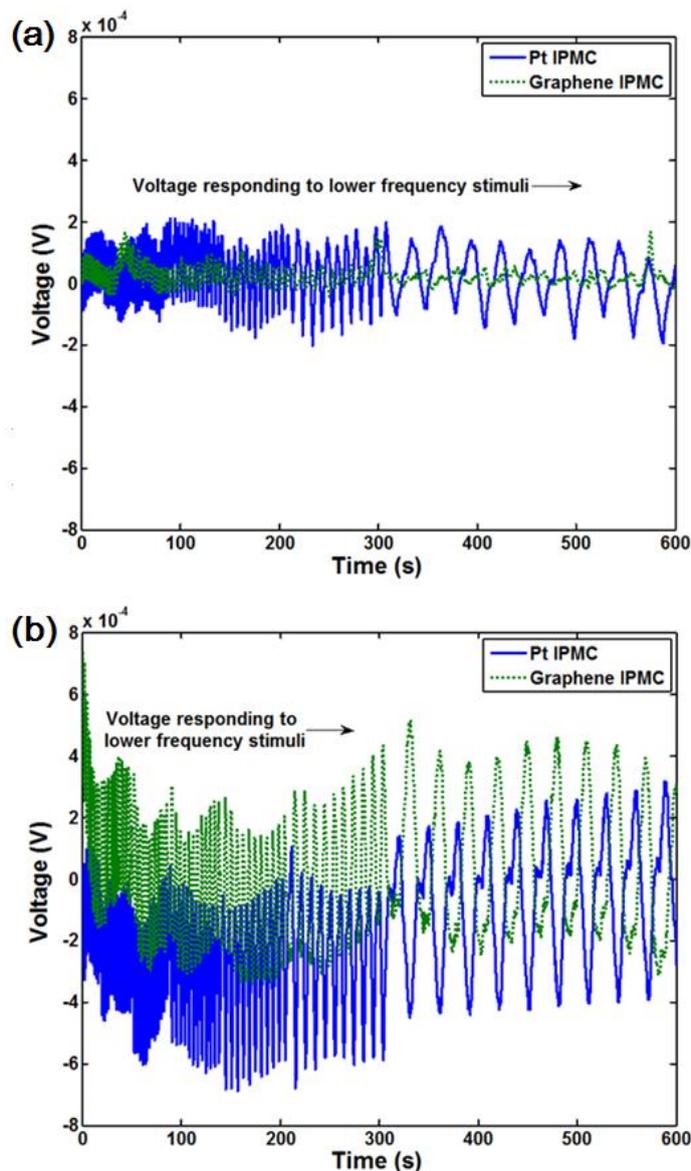
Figure 4. Performance comparison of the IPMC samples with the conductive graphene-based solution and Pt complex solution in air and seawater with the IPMC samples of 1 cm × 4 cm. (a) Voltages observed for the IPMC sample of the conductive graphene-based solution and Pt complex solution due to bending in air. (b) Voltages observed with the IPMC sample of the conductive graphene-based solution and the Pt complex solution utilizing both vertical waves and horizontal ocean currents in the seawater simulator

3.3 Marine physics investigation

For investigating both the strength and direction of ocean kinetics, we measured marine physics properties, such as waves and ocean currents, from the water surface to a depth of 10 m near the installation point (IP) for a 15-day observation period. The marine physics were investigated at the south sea research site (RS) of the Korea Institute of Ocean Science and Technology shown in Fig. 5(a). During the course of the experiments, the 15th typhoon called 'Kong-Rey' passed through the research site, which provided a good opportunity to determine the stability of the ocean kinetic energy

harvesting structure. Fig. 5(b) shows the flow velocities and directions of seawater measured at the surface, middle and bottom by an acoustic Doppler current profiler (ADCP).
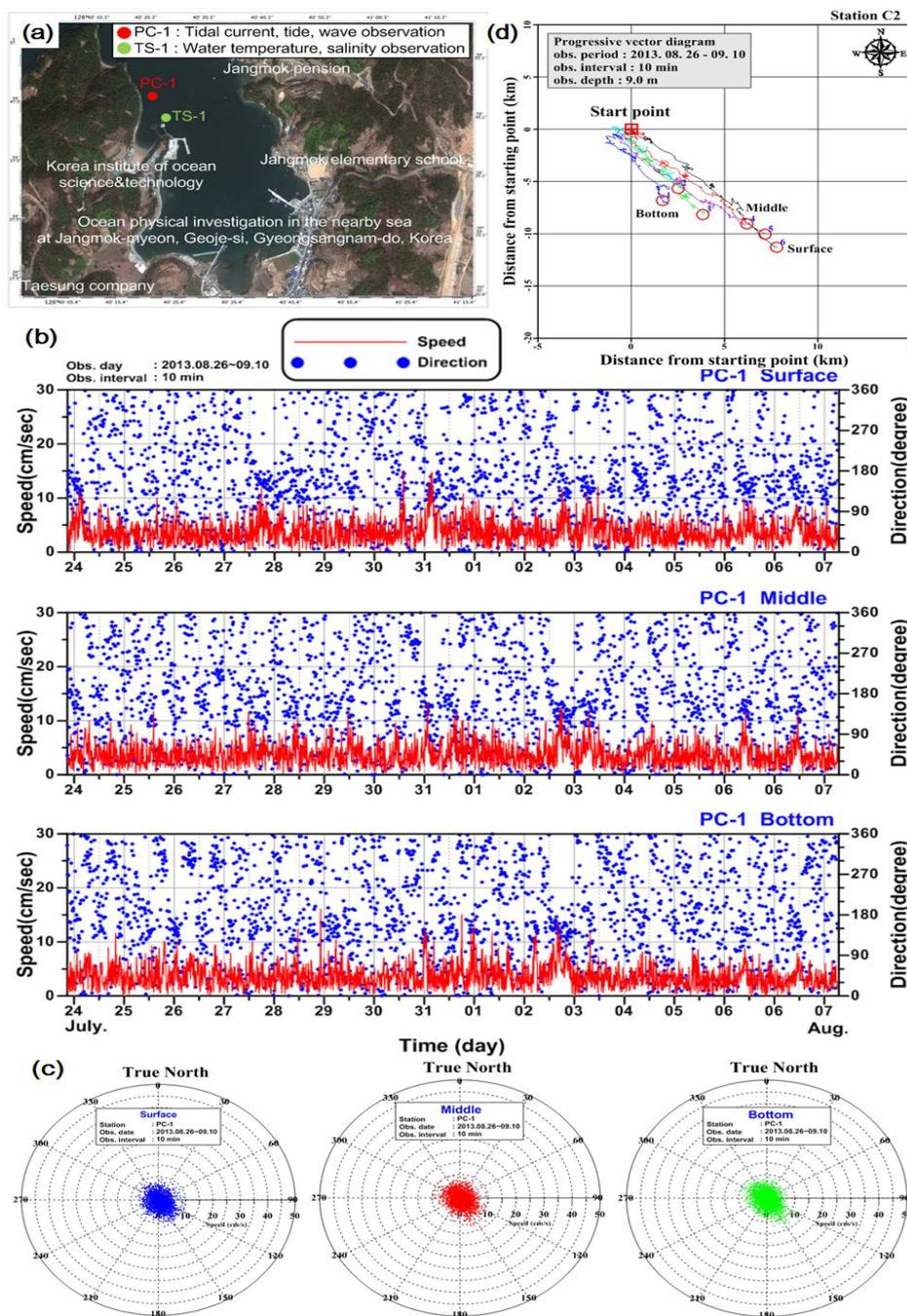
Figure 5. Marine physics investigation results near the installation point. (a) Location map for the south sea research site associated with the Korea Institute of Ocean Science and Technology where the marine physics were investigated. (b) Velocities and directions of seawater at the surface, middle and bottom measured by ADCP. (c) Flow velocities and directions at the surface, middle and bottom at the research site. (d) Progressive vector diagrams of ocean currents analyzed at the surface, middle and bottom for a 15-day observation period.

From the statistical analysis of the raw data obtained with the ADCP [24], the maximum flow velocities at the surface, middle and bottom were 15.1 cm/s, 13.4 cm/s and 16.1 cm/s, respectively, and the flux emergency rates under 10 cm/s at the surface, middle and bottom were 99.1%, 99.3% and 98.7%, respectively. In addition, the emergency rates for the south direction flow at the surface, middle and bottom were 61.9%, 57.6% and 56.2%, respectively, while the emergency rates for the north direction flow at the surface, middle and bottom were 38.2%, 42.4% and 43.8%, respectively. Therefore, the emergency rate of the south direction flow was higher than that of the north direction flow, as shown in Fig. 5(c). Based on ISO tidal analysis [24], the progressive vectors of the ocean currents are calculated at the surface, middle and bottom for a 15-day observation period, as shown in Fig. 5(d).

3.4 Performance test of ocean kinetic energy harvesting module

The ocean kinetic energy harvesting module, shown in Fig. 6(a), produced electrical energy after installation at the IP on August 24, 2013. The main buoy measured the electrical energy harvested with the module. Fig. 6(b) shows the extremely variable data obtained over 5 weeks starting on September 5, 2013 and continuing for 35 days. The module produced electrical energy over the target of 120 Wh and up to 600 Wh for approximately 10 days in the graph and approximately 20 days from the initial installation. The electrical energy produced gradually decreased to less than 120 Wh.

The instantaneous power density of IPMC with platinum electrodes of 10 mm (width) $\times$ 50 mm (length) $\times$ 0.2 mm (thickness) for tip excitation was measured to be around 45 W/cm^3 in air. The electrical energy target of 120 Wh is converted to the instantaneous power density of approximately 267 W/cm^3 which is greater than around 45 W/cm^3 in air [19]. Sodium ions, which are surrounded by free water molecules, move to the anode. Selective ionic and water transport across the polymer under an electric field result in volumetric changes, which promotes the energy harvest. The electrical energy at approximately day 10 significantly decreased because it is estimated that the kinetic energy of the waves and ocean currents is weak in the ocean. The growth of algae and barnacles on the module retard the IPMC bending motion and disrupt harvesting of the electrical energy, as shown in Fig. 6(c).

In comparison to mechanical wave energy converter (WEC) for converting the energy in ocean waves into electric power, research on electrochemical WEC has been limited thus far. IPMC material is a class of innovative electroactive polymer that produces electrical energy due to bending motion in a simple cantilever configuration. IPMC is hydrophilic and was studied as an underwater harvester based on flutter. We designed a movable power system utilizing both vertical waves and horizontal ocean currents for a sensor-level powered IPMC material using an electrochemical material consisting of IPMC to supply electricity to stand-alone offshore plants.
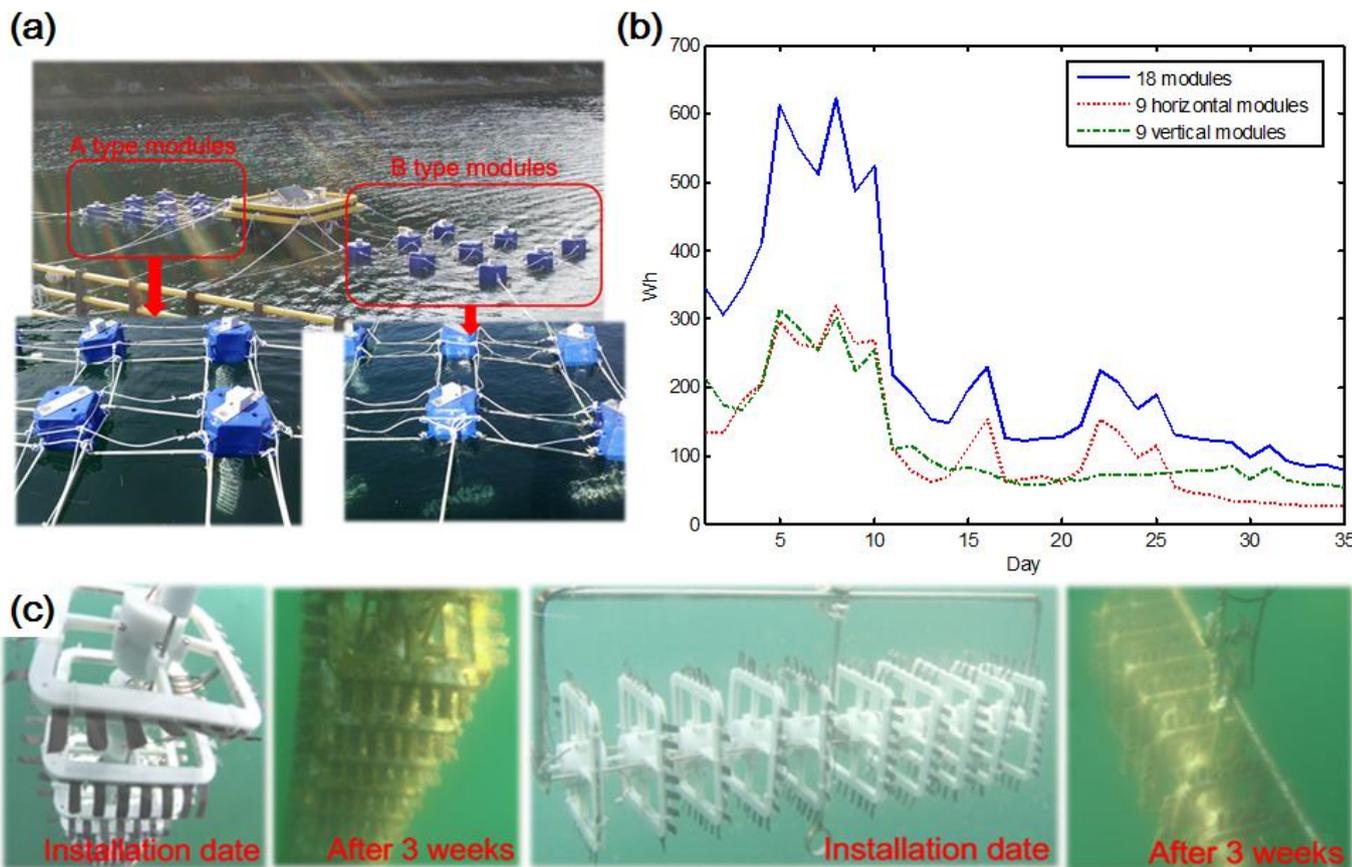
Figure 6. Performance of the ocean kinetic energy harvesting module with the conductive graphene-based solution IPMC. (a) Photograph of the ocean kinetic energy harvesting module. (b) History of the electrical energy harvested with the ocean kinetic energy harvesting module from ocean currents and waves. (c) Photographic comparison of the vertical and horizontal components between the day of installation and after 3 weeks.

4. CONCLUSIONS

To generate electricity from the kinetic energy in the ocean, we developed the world's first movable ocean kinetic energy harvesting module with an electrochemical material consisting of IPMC that replaces fixed tidal power generation to drive turbines using ocean flow. Ultimately, we constructed a movable module for stand-alone offshore plants such that the power grid is out of reach to accommodate situations that require reduced costs and expanded coverage.

During the course of our experiments, we encountered unexpected growth of algae and barnacles that affect electrochemical conversion with IPMC. Therefore, our goal is to develop a material or a structure that coexists with the ocean, which is a complex three-dimensional world, and would advance both conservation and development of marine resources.

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