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Polymer Complexes for Electrocatalytic Oxygen Evolution

Electrocatalytic water oxidation for oxygen gas evolution has been widely studied from the perspective of sustainable technology. However, the use of organic polymers as catalyst layers for this reaction remains undeveloped. We discuss, here, the prerequisites, characteristics, and advantages of π-conjugated polymers as electrochemical catalysts to modify anodic current collectors for water oxidation, including some examples by citing the previous works in literature. In section 3, we present our latest results, the use of an organic polymer complex of poly(ethylenedioxythiophene) and phytic acid supported by a hydrophilic poly(hydroxyethyl methacrylate) platform, which efficiently generates oxygen gas through anodic water oxidation.

Keywords: polymer complex, π-conjugated polymer, electrocatalyst, water oxidation, oxygen evolution, hydrophilic polymer, polythiophene, phytic acid.

Introduction

Water-splitting reaction to produce hydrogen and oxygen gases is one of the pinnacles of sustainable chemistry, and numerous efforts have focused on the electrocatalytic production of hydrogen and oxygen from water reduction and oxidation, respectively [1–7]. In addition to hydrogen production, the reductive process can follow other pathways, such as the reduction of nitrogen and carbon dioxide to produce ammonia, ethylene, ethanol, and propanol. Although the final targets are clean hydrogen and feedstock production for applications in sustainable energy and chemical industries, respectively, it is equally important to oxidize water into oxygen to balance and proceed with the counter-reductive reactions. The product of this reaction, oxygen, is the top three commodities and essential chemicals that are widely used in key oxidation reactions in chemical manufacturing, facilitated combustion, medical and respiratory care, wastewater treatment, and fish farming [8].

To generate oxygen from water, the catalysts for the electrochemical anodes have been extensively studied using molecular metal complexes, precious metal oxides, transition metal oxides, sulfides, and phosphides, as well as carbon and doped carbon materials [2, 9]. Catalysts that are used in catalytic processes with water at the polymer interface coated on a current-collecting anode substrate are of great interest; however, they remain at the early stage of development at present. These catalysts are advantageous for molecular engineering of organic polymers because they can modulate the electronic π-conjugated structure and the high hydrophilic surface area at the reaction front with water. Polymer-based catalysts are also attractive in film-forming processability, unlimited resources, non-toxicity, and chemical stability in acid/alkaline conditions.

The requirements for polymers with electrocatalytic water-oxidation capability involve the following: (i) a catalytic site for the water-oxidation reaction, (ii) an electrically conducting, three-dimensional network from the anodic substrate toward the reaction front, and (iii) a hydrophilic micro- and nanostructured scaffold for the pathways of reactant water molecules and product oxygen (microbubbles). A quick and effective method for examining such catalytic platforms is to use polymer complexes because they have been known to produce micro- and nanostructured functional polymers with hydrophilic/hydrophobic controlled properties. Bekturov et al. discussed a wide variety of polymer complexes approximately a half-century ago and summarized their findings [10, 11] with those of related fields [12, 13]. Some of these have prompted the practical application of polymer complexes in biomedical and nanomaterial fields [14–16]. For example, Kudaibergenov et al. successfully studied polymer complexation in oil engineering processes [17]. Furthermore, polyelectrolyte complexes and organic π-conjugated molecules have been extensively studied for dye fixation [18, 19]. Conductive hydrogels have been intensively studied for use in sensors and biomedical devices because fibrous assemblies of conjugated polymers create conducting network within hydrophilic scaffolds [20–22]. The application of conducting hydrophilic polymer complexes as electrocatalysts for water oxidation is expected to attract considerable interest.

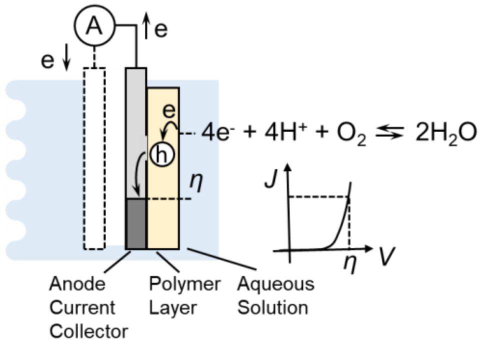

Figure 1. Energy-level diagram for the polymer-modified anode and water oxidation/oxygen evolution reaction and current density (*J*) curve for the oxygen evolution reaction; η is the overpotential to achieve the *J*

This article describes the theoretical background and chemical design of the electrochemical water oxidation to evolve oxygen gas in Section 1, as well as the characteristics of a series of electrocatalysts. In Section 2, we discuss the advantages and unsolved issues of organic (metal-free) π-conjugated polymers to modify the anodes for water oxidation by referring to recent works. Then in Section 3, our latest study on an electrocatalytic polymer is presented by using the polymer complex system composed of a conjugated polymer, a multivalent acid, and a hydrophilic polymer for efficient water oxidation. Finally, the perspectives are given for the emerging subject of facile water oxidation for on-site oxygen gas evolution.

1. Electrocatalytic water oxidation for oxygen gas production

Electrocatalysts play a key role in anodic water oxidation to generate oxygen and have been extensively studied in water electrolysis processes. While the cathodic reduction of protons or water to produce hydrogen involves a two-electron reaction, anodic water oxidation follows a four-electron/proton-coupled reaction (Fig. 1) and is more sluggish with a higher overpotential to overcome the kinetic barrier of the reaction than cathodic reductive reactions [9]. The oxygen evolution reaction is regarded as the rate-determining step or bottleneck for water-splitting reaction and reductive conversion to produce important feedstocks, which is hampered without an efficient oxygen-evolution catalyst. RuO_2 and IrO_2 exhibit excellent activity for water oxidation; however, both catalysts are made of precious metals and are chemically unstable during anodic operation and degraded into their per-oxidized forms [23]. Sustainable research has been devoted to developing electrocatalysts, with appropriate activity, composed of low-cost and widely available transition metal oxides such as MnO_x [24]. Attention has also been paid to carbon materials, including nanostructured carbons such as graphene and nanotubes. Heteroatom-doped carbon materials, such as N-, O-, and P-doped carbons, have recently emerged as promising electrocatalysts; however, their preparation is energy-consuming [25]. It is worth noting that these carbon materials might be unstable and oxidized to carbon dioxide at > 0.9 V vs. reversible hydrogen electrode (RHE).

Few studies have been reported on metal-free, organic-based electrocatalysis for oxygen evolution reactions, presumably because of their poor chemical stabilities under critical positive potential applications or oxidative conditions. Figure 1 shows the energy-level diagram of the polymer-modified anode for the oxidative reaction of water. Under the application of an anodic bias with a current collector, electrons are removed from the polymer layer to form a partially oxidized (doped) derivative (or hole formation), which successively extracts electrons from water molecule to oxidatively produce oxygen gas. The polymer catalytically mediates electron transfer from the water molecules to the anodic current collector; thus, it is more mediation-active, and the smaller bias or overpotential, η, (vs. the reaction equilibrium potential) promotes oxygen production.

2. Water oxidation using the polymer-modified anodes

Polyimides are thermo- and chemically stable and mechanically tough engineering plastics. Polyimide modification as a durable organic polymer-modified anode for efficient water oxidation to produce oxygen was reported by Li et al. [26]. They prepared poly(*p*-phenylene pyromellitic diimide) (PPPI, **1** in Figure 2) with a large and rough surface via in situ condensation after coating a solvent-soluble precursor polymer on carbon cloth (CC). Electrical impedance analysis indicated appropriate conductivity of the polyimide layer up to a thickness of 200 nm. Scanning electron microscopy (SEM) images and X-ray photoelectron spectroscopy revealed the metal-free and porous features of the polyimide layer coated on the substrate (the porous surface was attributed to the removal of water during polycondensation). The polyimide/CC worked as a durable and effective anode over a wide pH range, with an anodic current density (J) of 10 mA/cm^2 at a potential of 1.7 V vs. RHE, which was only 110 mV higher than the working potential of the benchmark IrO_2/CC electrode (Figure 3(*a*)). A large J was obtained in an alkaline pH 13 solution with 99 % of Faraday efficiency. The smaller Tafel slope of 75 mV/dec, compared to that of IrO_2 (87 mV/dec, Figure 3(*b*)), indicated favorable reaction kinetics (CC as an effective current collector and imide group as a potential catalytic site). The Tafel slope (log J vs. the given potential) reflects the activity of the electrode material or the activation energy of the redox reaction at the electrode-solution interface, in which smaller slopes indicate better reaction kinetics. In addition, the polyimide/CC can be processed into a desired shape for practical use, including as a mechanically-tough flexible electrode.

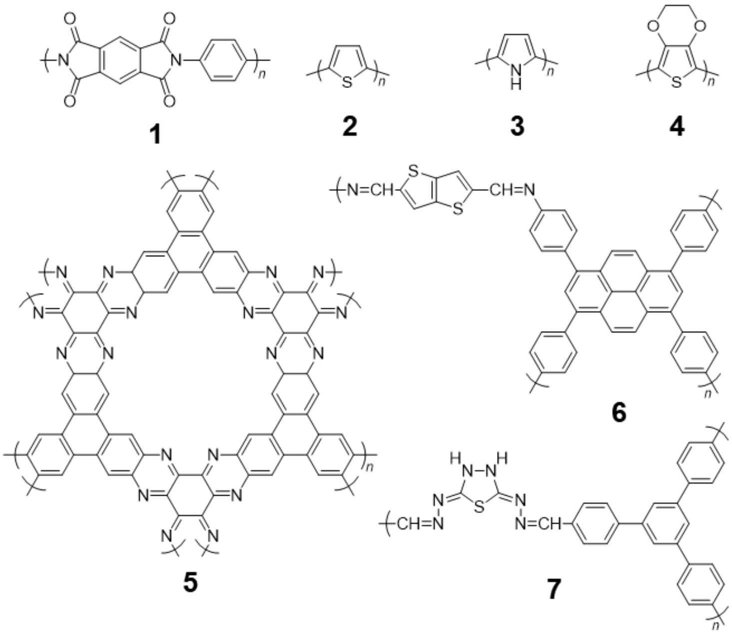

Figure 2. Chemical structures of π-conjugated polymers used to modify the anodic current collector

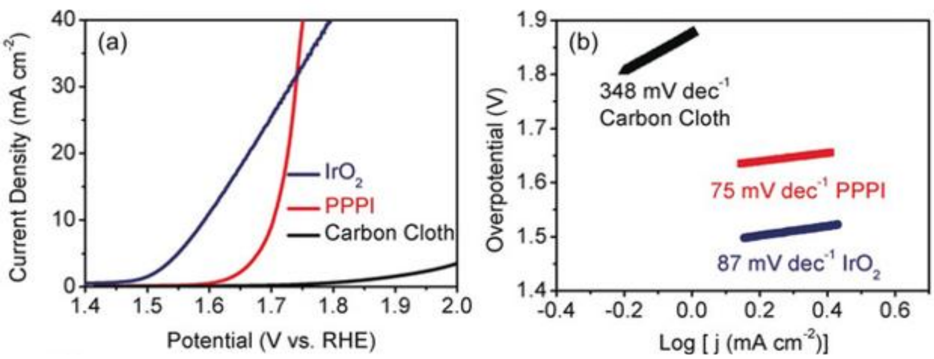

Figure 3. Water oxidation performance: (*a*) the anodic J and (*b*) Tafel slope of the poly(phenylene pyromellitic diimide) (PPPI)/CC and the benchmark IrO_2 (Copyright from Wiley-VCH 2018: Ref. 26))

Li et al. also prepared polythiophene (**2** in Figure 2) on an O-doped CC via electro-polymerization of thiophene [27]. The tough polythiophene layer with a thickness of 26 nm strongly adhered to carbon without detachment during the subsequent oxidative process. The polythiophene/O-doped CC anode worked as water oxidation catalysts to evolve oxygen. Its J reach up to 24 mA/cm^2 at 1.7 V vs. RHE in pH 13, which was twice that of the benchmark IrO_2 catalyst. The low overpotential and small Tafel slope of 61 mV/dec indicate the catalytic capability of the polythiophene/O-doped CC. The S 2p X-ray photoemission spectroscopy results suggested efficient redox catalysis of the thiophene, presumably involving a redox reaction between the sulfur and sulfone groups, which were strongly coupled with the O-doped carbon surface.

Zhang et al. designed a two-dimensional (2D) covalent organic framework composed of highly conjugated structures with appropriate carbon and nitrogen stoichiometry through DFT calculations [28]. Thermal condensation of triphenylenehexamine and hexaketocyclohexane yielded a phenazine-linked basal plane framework with a C_4N composition (**5** in Figure 2). The crystalline-like framework was nanoporous, chemically robust, and exhibited water oxidation activity in an alkaline solution, with a J of 10 mA/cm^2 and a Tafel slope of 64 mV/dec. Carbon sites around nitrogen atoms in the conjugated structure are presumed to be the catalytic sites for the oxygen evolution reaction.

To achieve a current density of 10 mA/cm^2 and a Tafel slope of <100 mV/dec, Chen et al. wrapped a carbon nanotube with a conjugated 2D thiophene polymer connected to pyrene (**6** in Figure 2), which acted as an electrochemical water oxidation catalyst to evolve oxygen in an alkaline solution [29]. Jena et al. reported a covalent organic 3D framework that was prepared with a π-conjugated network of thiadiazole and triphenylbenzene (**7** in Figure 2) on a glassy carbon substrate. This exhibited electrocatalytic oxygen evolution activity with an onset of 250 mV and a J of 10 mA/cm^2 in an alkaline solution [30]. The low Tafel slope of 40 mV/dec and Faraday efficiency of 98 % were attributed to the oxidation pathway of four-electron oxidation. The π-conjugated network with a porous structure allows for fast charge and reactant transfer processes, and the catalytic activity per mass can reach up to 286 mA/mg.

He et al. prepared polypyrrole (**3** in Figure 2) doped with phytic acid (or inositol hexaphosphoric acid) on CC as a conductive hydrogel with efficient water oxidation electrocatalytic activity [31]. Pyrrole was oxidatively polymerized in situ on the CC in the presence of phytic acid. SEM images showed the formation of nanoparticles with a diameter of ca. 15 nm, which were interconnected to form a fibrous network on the carbon substrate. Spectroscopic analyses revealed the partial oxidation and homogeneous complexation of polypyrrole or doping with phytic acid with an optimum molar ratio of six. The contact angle of the water droplet was almost zero, indicating a super hydrophilic nature of the polymer complex. The polypyrrole-phytic acid/CC displayed water oxidation activity in an alkaline pH 10 solution with a high J and a low onset potential of 1.51 V vs. RHE, whereas both the polypyrrole without phytic acid and the CC substrate itself were negligible. A large J of 110 mA/cm^2 (for the cloth) was observed with a small Tafel slope of 55 mV/dec. Through DFT calculations, the phytic acid complexed with the doped polypyrrole was found to be involved with positively charged cyclohexane carbons, which are presumed to be the catalytic active sites. The doped polypyrrole was electrically conductive, forming a fast charge transfer network during water oxidation. The authors summarized a new direction for molecular/polymer-complex-based electrocatalysts formed on carbon substrates with high surface areas.

3. PEDOT–Phytic acid complex and its water oxidation activity

Poly(3,4-ethylenedioxythiophene) (PEDOT, **4** in Figure 2) is a representative conjugated polymer that is doped or oxidized with four (or more) thiophene units in the conjugated backbone to stabilize or store one hole or positive charge (doping level of ca. 25 %) accompanied by one counter anion compensation [32]. One of the typical counter acids (or anions) to complex with the positive charge of PEDOT is poly(styrene sulfonic acid) (PSS), forming a polyelectrolyte complex of PEDOT-PSS, which are commercially available as aqueous suspensions [33]. A variety of small-molecule acids can also be used as counter acids, including toluene sulfonic acid, perchloric acid, tetrafluoroboric acid, and trifluoroacetic acid. Among them, phytic acid (PA), six phosphonic acid-substituted cyclohexane, is a multivalent acid derivative that acts as a strong cation chelator that can suppress metal absorption into the human body [34]. In addition, PA was used in a polyaniline complex to produce a conductive hydrogel [35]. Meanwhile, poly(2-hydroxyethyl methacrylate) (pHEMA) is a hydrophilic polymer that adheres well to any substrate and is widely used as a platform for biomedical applications [35].

Herein, we focus on the combination of PEDOT, PA, and pHEMA, as a conducting polymer, chelating or complexing agent, and hydrophilic scaffold, respectively, to study its properties as an organic-based water oxidation electrocatalyst.

PEDOT-PSS water dispersion (Heraeus, CLEVIOS™ P VP Al 4083) and an ethanol solution of pHEMA (Sigma-Aldrich, average molecular weight: 3×10^5) were dropped on CC (Toyo Co., EC-CC1-060) as a current-collecting substrate and annealed for several hours at 120 °C to yield the conducting PEDOT coating. Without pHEMA, the PEDOT was directly delaminated from the CC substrate. pHEMA also caused a significant decrease in the surface hydrophilicity and contact angle of the PEDOT/pHEMA-modified CC (lower of Figure 4*b*). The thickness of the polymer layers was 300 nm. The obtained hydrophilic PEDOT/pHEMA/CC substrate was then immersed in an aqueous solution of PA (TCI). During this process, some PSS was eluted from the aqueous solution, which was confirmed by absorption spectroscopy. PA was irrigated into PEDOT-PSS and PSS was removed to form an effective PEDOT-PA complex through multivalent ionic interactions.

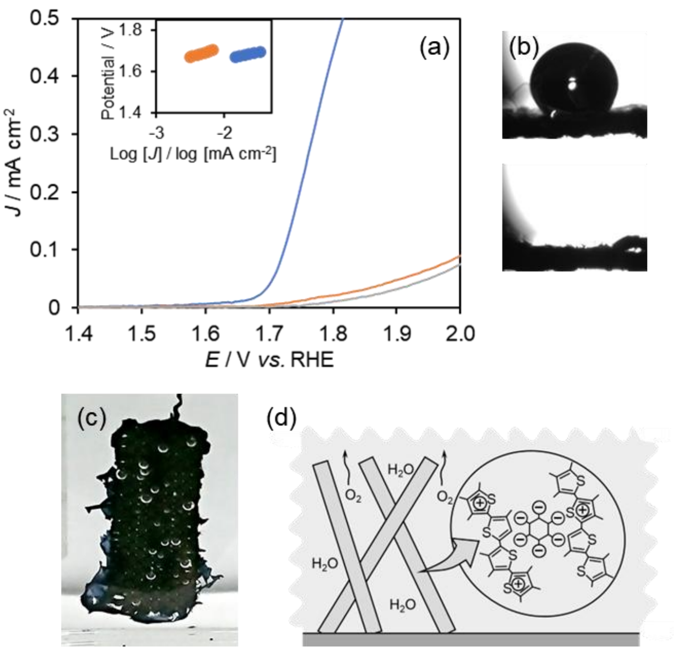

Figure 4. Water oxidation performance: (*a*) the anodic *J* and (inset) Tafel slope of the PEDOT-PA/pHEMA complex (blue), and PEDOT/pHEMA (red), and CC (gray), (*b*) Contact angle of (upper) CC substrate and (lower) PEDOT-PA/pHEMA-modified CC, (*c*) the PEDOT-PA/pHEMA complex during the anodic operation, and (*d*) Schematic image of the PEDOT-PA/pHEMA complex

The electrocatalytic performance of PEDOT-PA/pHEMA/CC was studied in an aqueous solution (pH 12) by linear sweep voltammetry using a potentiostat/galvanostat (Hokuto Denko, HZ-7000). Under anodic potential application, *J* for the PEDOT-PA/pHEMA complex can reach up to approximately 0.5 mA/cm^2 (Figure 4*a*), with an onset oxidation potential of 1.7 V vs. RHE. The anodic current corresponds to an oxidative reaction or water oxidation, and oxygen bubbles were continuously observed at the anode (Figure 4*c*). The *J* values for the PEDOT/pHEMA and CC substrate remained low, and the activity of the CC substrate immersed in the PA solution was also small, as in the control experiments. A small Tafel potential slope of 69 mV/dec was observed for the PEDOT-PA/pHEMA complex (inset of Figure 4*a*) in comparison with that for PEDOT/pHEMA. These results demonstrate the high activity of the PEDOT-PA/pHEMA complex layer for water oxidation to generate oxygen from water.

Figure 4*d* illustrates the PEDOT-PA/pHEMA polymer complex as a water oxidation electrocatalyst. The multivalent acidic PA ionically interacted with PEDOT to provide a partially doped (positively charged) PEDOT-fibrous pathway for electric conduction and to form a catalytic site. pHEMA immobilized the PEDOT-PA complex on the current collector and provided a hydrophilic platform for the water oxidation/oxygen evolution reaction. Overall, a simple complexation of the well-known PEDOT, PA, and pHEMA as a conductive polymer, chelating reagent, and hydrophilic polymer, respectively, successfully yielded an organic-based electrocatalyst for water oxidation to generate oxygen gas.

Conclusions

π-Conjugated polymers contain positive charges (holes) upon complexation with counter anions (doping). These holes are characterized by long lifetimes and tunable energy levels, which could mediate water oxidation in anodic potential applications. Organic-based polymer complexes composed of electrically conducting networks of conjugated polymers in the hydrophilic polymer platform for the reactant/product (water molecule/oxygen gas) pathway are possible metal-free, sustainable electrocatalyst candidates for facile water oxidation to generate oxygen in any decentralized location.

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Х. Шинохара, Х. Нишиде

Оттегінің электрокаталитикалық бөлінуіне арналған полимерлік комплекстер

Оттегі газын шығару үшін судың электрокаталитикалық тотығуы тұрақты технологиялар тұрғысынан кеңінен зерттелген. Дегенмен, бұл реакция үшін катализатор қабаттары ретінде органикалық полимерлерді пайдалану әлі дамымаған. Мақалада π-түйіндес полимерлерді судың тотығуында анодтық токалғышты модификациялау үшін электрохимиялық катализатор ретінде пайдаланудың негізі, сипаттамалары және артықшылықтары, соның ішінде алдыңғы жұмысқа сілтемелері бар кейбір мысалдар қарастырылған. Үшінші бөлімде судың анодты тотығуы арқылы газ тәрізді оттегін тиімді генерациялайтын гидрофильді поли(гидроксиэтилметакрилат) платформасымен қамтамасыз етілген поли(этилендиокситиофен) және фитин қышқылының органикалық полимер кешенін қолдану бойынша авторлардың соңғы зерттеулерінің нәтижелері берілген.

Кілт сөздер: полимер кешені, π-түйіндес полимер, электрокатализатор, судың тотығуы, оттегінің бөлінуі, гидрофильді полимер, политиофен, фитин қышқылы.

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Полимерные комплексы для электрокаталитического выделения кислорода

Электрокаталитическое окисление воды с целью выделения газообразного кислорода широко изучено с точки зрения устойчивых технологий. Однако использование органических полимеров в качестве каталитических слоев для этой реакции остается неразработанным. В данной статье обсуждены предпосылки, характеристики и преимущества применения π-сопряженных полимеров в качестве электрохимических катализаторов для модификации анодных токосъемников при окислении воды, включая некоторые примеры с литературными ссылками на предыдущие работы. В разделе 3 представлены результаты последних исследований авторов по использованию органического полимерного комплекса поли(этилендиокситиофена) и фитиновой кислоты, поддерживаемого гидрофильной поли(гидроксиэтилметакрилатной) платформой, который эффективно генерирует газообразный кислород посредством анодного окисления воды.

Ключевые слова: полимерный комплекс, π-сопряженный полимер, электрокатализатор, окисление воды, выделение кислорода, гидрофильный полимер, политиофен, фитиновая кислота.

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