Ce(III)-Based Coordination-Complex-Based Efficient Radical Scavenger for Exceptional Durability Enhancement of Polymer Application in Proton-Exchange Membrane Fuel Cells and Organic Photovoltaics

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1. Introduction

To ensure a sustainable future, a tremendous range of energy conversion and storage devices including fuel cells, photovoltaics, and electrolyzers, has been developed in recent decades for the eco-friendly production and consumption of energy, without increasing CO₂ emissions.[1] The main concern about those devices for practical realization is maximizing the overall lifetime of their operation, which is largely affected by the durability of device-configuring materials under the specific operation condition for each device. In particular, soft polymeric materials are some of the key materials in those devices and are widely applied as active sites for energy conversion, charge carrier transporting media, material transporting media, etc. However, degradation of those polymeric materials in the device inevitably occurs during device operation in physical and chemical manner.[2] To be more...
specific, chemical degradation of polymers, collapse of active moieties or backbones in the polymer structure significantly reduce the overall durability of the device. One of the critical reasons for chemical degradation is the generation of highly reactive radical species including oxygen radicals such as superoxides (\(O_2^−\)), peroxyhydroxyl radicals (\(\cdot\text{OOH}\)), hydroxyl radicals (\(\cdot\text{OH}\)), etc., which inevitably occurs due to light irradiation or unwanted side reactions in the device.[15] Those highly reactive species severely attack and chemically degrade the polymeric materials in the devices, and seriously impair the overall stability of the energy conversion and storage devices.[16] Therefore, alleviating the chemical degradation of the active polymer materials caused by radical is of great importance to improve the overall stability of device applications.

The addition of radical scavengers has been reported to be an effective strategy to improve the chemical resistivity of active materials to radical species in energy conversion and storage devices. The additive radical scavengers rapidly react with the generated radical species during device operation before they can attack the active polymer structures in the energy conversion and storage device. Several radical scavengers have been investigated for their therapeutic potential. Among the candidates, Ce-based radical scavengers (either free ions or surface states from CeO2 nanoparticles) have been accepted as one of the most promising inorganic radical scavengers because of high radical scavenging activity based on their redox properties of the Ce\(^{3+/4+}\) switch and coupling.[17] However, the mechanisms of the additives in scavenging radicals are very strongly affected by environmental parameters and interactions. Indeed, a number of additive radical scavengers employed in the device typically diminish the initial device performance by forming unprecedented disadvantageous interactions with the polymeric materials.[18] At the same time, the reactivity of radical scavenging and the self-regeneration reaction of free Ce\(^{3+}\) ion-based radical scavengers has been also shown to vary under device operating conditions in many studies,[5–7] thereby limiting the use of those Ce-based radical scavengers for the practical application.

In this study, we report that a coordination complex of Ce can be applied as an effective, and universally applicable radical scavenger for energy conversion and storage devices. We explored several Ce-based coordination complexes with different chelating ligands (dipicolinate, picolinate, and acetylacetonate), which can show stabilizing effect of the Ce\(^{3+}\) ion center as well as modification of redox properties of the Ce\(^{3+/4+}\) redox couple to enhance radical scavenging efficiency of the Ce\(^{3+}\) ion center. Among those complexes, the Ce\(^{3+}\)-dipicolinate coordination complex showed \(\approx\)3.5 times higher electrochemical redox response toward hydroxyl radicals compared to the free Ce\(^{3+}\) ion. In an electrochemical energy conversion device, a proton exchange membrane fuel cells (PEMFCs), the addition of the coordination complex-based radical scavenger critically improved overall durability without decreasing initial device performance, in contrast to a free Ce\(^{3+}\)-ion-based radical scavenger (Ce salt), which lowered the initial performance. Moreover, the Ce-based coordination complex radical scavenger enhanced the durability of an organic photovoltaic (OPV) device, without any initial performance drop, showing the potential of the Ce-based coordination complex as a universally applicable radical scavenger for energy conversion devices.

2. Results and Discussions

2.1. Synthesis and Characterization of the Radical Scavenging Activity of [Ce(dipic)]\(^3+\)

We conjectured that a Ce-based coordination complex, where a central Ce ion is surrounded by coordinated ligands, could modify the redox property of the Ce\(^{3+/4+}\) couple by changing the local electron density around the Ce\(^{3+}\) species, thereby changing its radical scavenging efficiency. To prove our hypothesis, we prepared three Ce-based coordination complexes with different chelating ligands. First, the coordination complex \([\text{Ca}_3(\text{H}_2\text{O})_{12}\text{Ce}_2(\text{dipic})_6]6\text{H}_2\text{O}\) (1), with a Ce\(^{3+}\) is surrounded by three dipicolinate ligands containing \([\text{Ce}(\text{dipic})]^{3-}\) (dipic\(_2\) = dipicolinic acid) moiety, was synthesized according to the previous literature.[18] The dipicolinate ligand, a common pincer-type ligand, contains two carboxylic acid groups with a pyridine group in the middle which can be an excellent linker for the coordination networks. For comparison, a coordination complex containing bidentate picolinate ligands, \(\text{Na}_2[\text{Ce}(\text{pic})_5]·\text{picH}·4\text{H}_2\text{O}\) (2), with a Ce\(^{3+}\) is surrounded by five picolinate ligands containing \([\text{Ce}(\text{pic})]^{2-}\) (pic\(_2\) = picolinic acid), was also prepared.[19] We also characterized a commercially available Ce-based coordination complex, \(\text{Ce}(\text{acac})_3(\text{H}_2\text{O})_2\) (3) (acac = acetylacetonate), where three bidentate acetylacetonate ligands are coordinated to the Ce\(^{3+}\) center. The structural formula of the Ce-based complexes 1, 2, and 3 is summarized in Figure S1, Supporting Information. Also, the structures of the Ce-based coordination complexes 1, 2, and 3 were explored by a density functional theory (DFT) calculation method. Initial geometries were obtained from their corresponding X-ray crystal structures reported in the literature.[8,9] The structures were optimized at the same level of theory (6-31 G(d,p)), and the optimized structures are shown in Figure 1a.

The chemical properties of the Ce center in the coordination complexes were investigated by X-ray photoelectron spectroscopy (XPS) spectra of the Ce 3d level, as shown in Figure 1b. Because the distinctive peak structure from the Ce\(^{3+}\) state around 916.9 eV (\(\text{u}^\ast\)) was not observed in all complexes, the chemical state of the cerium in the three complexes mainly possessed the Ce\(^{3+}\) state.[10] Interestingly, a slightly negative shift of binding energy was observed in the peaks of complex 1 compared to complexes 2 and 3, which indicates a higher electron density around the Ce\(^{3+}\) center in complex 1 than other complexes. This originates from the property of the dipicolinate ligand, which strongly coordinates to the Ce\(^{3+}\) center in a tridentate fashion with two carboxylates and one pyridinic nitrogen as electron donors. In contrast, the picolinate ligand in complex 2 interacts with the Ce\(^{3+}\) center in a bidentate fashion, with one carboxylate and one pyridinic nitrogen. Moreover, because the electron density around the pyridinic nitrogen in the dipicolinate ligand is higher than that in the picolinate ligand,[11] the electron-donating property of the pyridinic nitrogen in the dipicolinate ligand is stronger than that in the picolinate ligand. The XPS spectra of the three complexes on the N 1s level (Figure 1c) were consistent with the Ce 3d XPS spectra, where the shoulder peak of higher binding energy was observed to be stronger in complex 1 than in 2, indicating a higher donation of electrons from ligand to metal center.
Then, we explored the Ce\(^{4+/3+}\) redox potential of Ce complexes 1 to 3 via a DFT-based method.\(^{[12]}\) For compounds 1 and 2, monomeric cerium moieties of [Ce(dipic)]\(^{3-}\) and [Ce(pic)]\(^{2-}\) were selected for calculation, and the initial geometry for structure optimization was taken from the reported crystal structure.\(^{[8,9]}\) The Ce\(^{4+/3+}\) redox potentials for Ce complexes

Figure 1. a) Density functional theory (DFT)-optimized structure of Ce complexes 1, 2, and 3. Light yellow, gray, red, blue, and white balls represent Ce, C, O, N, and H, respectively. b) Ce 3d and c) N 1s X-ray photoelectron spectroscopy (XPS) spectra of the Ce complexes 1, 2, and 3. d) DFT-calculated \(E_{1/2}\) values of Ce\(^{4+/3+}\) redox reaction of Ce complexes and cerium nitrate (CAN) salt. e) Cyclic voltammetry (CV) curves of the bare and Ce complex-modified screen-printed carbon electrode (SPCE) toward 10 mM of -OH from Fenton reaction. f) Calculated redox response obtained with different Ce salt or Ce complexes toward 10 mM of -OH from Fenton reaction normalized per mass of cerium on the electrode.
1, 2, 3, and ceric ammonium nitrate (CAN, [Ce(NO₃)₆]²⁻) were calculated against ferrocene (Fc⁺/Fc). The calculated redox potentials ($E_{\text{redox}}$) for 1, 2, and 3 were $-0.232, -0.002$, and $0.540$ $\text{V}_{\text{Fc+}/\text{Fc}}$, respectively, which were lower than that of CAN (1.344 $\text{V}_{\text{Fc+}/\text{Fc}}$). In other words, based on the calculation results, the Ce³⁺ state in complex 1 was more likely to be oxidized to the Ce⁴⁺ state among the Ce complexes or free Ce³⁺ ions, because it had the lowest calculated standard redox potential. Therefore, we hypothesized that the Ce³⁺ species in 1 are more prone to be oxidized, whereas the. The calculated $E_{\text{redox}}$ is much lower than the other Ce complexes or Ce³⁺ free ions, because the oxidation of the Ce³⁺ state toward the Ce⁴⁺ state can scavenge OH radical species by the following Equation (1). 

\[ \text{Ce}^{3+} + \cdot \text{OH} + \text{H}^+ \rightarrow \text{Ce}^{4+} + \text{H}_2\text{O} \] (I)

To confirm the high OH radical scavenging activity of the Ce complexes, the electrochemical reaction of a Ce complexes-modified screen-printed carbon electrode (SPCE) toward the OH radical was evaluated. Figure 1e shows the cyclic voltammetry (CV) of the Ce complexes-modified SPCE in 10 mM OH radicals generated from the Fenton reaction. The redox response of the electrode was calculated using the difference between the oxidation and reduction peaks from the reduction of the Ce complex and OH radicals and normalized by the mass of the Ce on the electrode. As shown in Figure 1f, coordination complex 1 showed the highest electrochemical redox response toward OH radicals (16.21 mA mgCe⁻¹), around 2.5, 3.1, and 3.5 times higher than that of complex 2 (6.53 mA mgCe⁻¹), 3 (5.26 mA mgCe⁻¹), and Ce salt (4.60 mA mgCe⁻¹), respectively. The trend in redox response toward OH radicals is consistent with the DFT-calculated redox potential in Figure 1d. Compared with the free Ce³⁺ ion, the increased local electron density around the Ce³⁺ center of the Ce complexes by chelating ligands – dipic, pic, and acac, facile redox reaction from Ce³⁺ to OH radical was enabled by the lowered standard redox potential, thereby increasing the electrochemical redox response. Based on the high OH response of the coordination complex compared with Ce salts, we employed the Ce-based coordination complexes as a radical scavenger additive in a PEMFC and an OPV device.

2.2. Application of Ce Complex Radical Scavenger in an Electrochemical Device

To use the Ce complex- and Ce salt-based radical scavengers in the PEMFC, the as-synthesized Ce complexes or Ce salts were introduced into the polymer electrolytes, and reinforced composite membranes (RCMs). In brief, a dispersion containing perfluorosulfonic acid (PFSA) solution and the Ce-based complexes was impregnated in a porous polytetrafluoroethylene (PTFE) film to fabricate the RCMs. The relative amount of Ce-based antioxidant added to the PFSA ionomer in the RCM was fixed to [Ce]/[SO₃] = 0.5%. To verify the uniform impregnation of the Ce complexes into the RCM, the colloidal stability of the PFSA/Ce complex 1 dispersion was investigated by UV–vis spectroscopy of the dispersion under the steady state for 24 h. As shown in Figure S2, Supporting Information, no significant change in UV–vis spectra of PFSA/Ce complex 1 dispersion was observed over 24 h, indicating that the Ce complex 1 could be well-dispersed in the PFSA ionomer solution. The thickness of the Ce complex-containing RCMs was 15 ± 1 μm (Figure 2a). Using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) elemental mapping analyses of the surface of the complex 1-based RCM (Figure S3, Supporting Information), the Ce and N contents of complex 1 were found to be well-distributed in the RCM, indicating that the Ce complex-based radical scavenger was uniformly dispersed in the PFSA ionomer solution. The effective concentration of sulfonate sites in the RCMs was estimated by measuring their ion exchange capacity (IEC). The IEC value of 1-based RCM was $1.05 \text{meq} \cdot \text{g}^{-1}$, slightly higher than that of pristine RCM ($1.01 \text{meq} \cdot \text{g}^{-1}$) and other complex-added RCMs (Figure 2b). In contrast to the Ce complexes, the addition of Ce³⁺ salt resulted in a decrease in IEC, due to the strong interaction between the free Ce³⁺ ions and sulfonate groups from the PFSA ionomer.

Furthermore, coordination complex 1 in the RCM showed superior antioxidant capability compared to Ce salt or other coordination complexes in the RCM. The radical scavenging performance of the Ce complexes or Ce salts in the RCM was assessed using an accelerated chemical degradation test, immersed in Fenton’s solution (a mixture of 3 wt% H₂O₂ and 2 ppm of Fe²⁺ solution to generate •OH radicals) at 80 °C. The radical attack results in the emission of fluoride ions from the polymer backbone of the PFSA. Therefore, we quantified the fluoride emission rate (FER) using the resulting Fenton’s solution every 24 h. As shown in Figure 2d, the addition of Ce complexes or salt to the RCM resulted in a decrease in FER compared to the pristine RCM, indicating the chemical stability of the RCMs was improved by the radical scavenging Ce complexes or salts. Among the RCMs, complex 1 containing RCM showed the lowest FER. At 24 h, the FER values of the 1-based RCM (0.0033 μmol cm⁻² h⁻¹) were 6.9 and 3 times lower than that of pristine RCM (0.0227 μmol cm⁻² h⁻¹) and Ce salt-based RCM (0.0100 μmol cm⁻² h⁻¹), respectively. In contrast, the FER values of the complex 2 and 3-based RCMs were higher than that of the [Ce(dipic)₃]³⁻–based RCM, indicating the lower performance of those complexes as radical scavengers. Moreover, the trends in FER did not change over 72 h of chemical stability tests; the [Ce(dipic)₃]³⁻–based RCM exhibited a lower FER than the other RCMs. This clearly indicates that the addition of the Ce complex, [Ce(dipic)₃]³⁻–based RCM improved the chemical stability of RCM against a harsh chemical environment, by removing detrimental radical species.

Then we investigated the PEMFC performances of the RCMs containing complex 1 and Ce salt at 80 °C, at RH 100% condition. The PEMFC polarization curves (Figure 3a,b) showed that the cell performance of the Ce complex 1-based RCM was superior to the Ce salt-incorporated RCM. The 1-based RCM exhibited 1.965 A cm⁻² of current density at 0.6 V of cell voltage (j₀.6v), which was slightly higher than that of pristine RCM (1.845 A cm⁻²) even with the addition of antioxidant. However, the addition of Ce salt (1.698 A cm⁻²) resulted in a
decrease in cell performance (Figure 3c). Also, as shown in Figure 3d, the 1-based RCM exhibited a higher maximum power density \( (p_{\text{max}}) \) value of 1.302 W cm\(^{-2}\) than the pristine RCM (1.253 W cm\(^{-2}\)), while incorporating the Ce salt resulted in a cell performance drop, and \( p_{\text{max}} \) value of 1.168 W cm\(^{-2}\). In contrast to the adverse effect on single-cell performance with the addition of Ce salts into the RCM, a PEMFC cell performance drop was not observed when complex 1 was added into the RCM. This can be attributed to the higher IEC and \( \sigma_{\text{H}^+} \) value of the 1-based RCM, compared with the Ce salt-based RCM. Based on the chemical formula, [Ce(dipic)\(_3\)]\(^{3+}\), the negatively charged complex 1 would not strongly interact with \(-\text{SO}_3\text{H}\) groups in the PFSA ionomer, thereby would not block the proton-transporting sites. In contrast, the strong interaction between positively charged free Ce\(^{3+}\) ions and negatively charged sulfonate groups in the PFSA ionomer significantly blocks the proton transporting pathway in the RCM, which results in higher resistance than the 1-based RCM, affecting overall single cell performance. The EIS spectra of the membrane electrode assemblies (MEAs) (Figure S4, Supporting Information) measured at 80 °C, RH 100% corroborated the cell performance trends, which demonstrated that the resistance of the 1-based MEA was lower than that of the Ce salt-based MEA due to the higher dispersion of complex 1 in the RCM. The 1-based RCM also exhibited superior PEMFC single cell performance in the low humidity condition; the PEMFC polarization curves (Figure S5, Supporting Information) of pristine, Ce salt-, and 1-based RCM measured under low humidity (80 °C, RH 50%) showed trends similar to the polarization curves under the 80 °C, RH 100% condition.

Next, to demonstrate the efficient radical scavenging ability of 1, accelerated durability testing (ADT) of the cell was conducted using an open-circuit voltage (OCV)-holding durability test protocol, under the low humidity condition (90 °C, RH 30%, \( \text{H}_2/\text{air} \) 150 kPa), which represents a harsh environment with the rapid formation of radicals. Figure 3e shows the change in OCV after 120 h. A gradual degradation of the OCV of each cell was observed during the ADT. The OCV degradation rate of the RCM was calculated by the linear fitting of each OCV curve after 24 h (linear region). The OCV of the pristine RCM dropped from 0.950 to 0.792 V over 120 h at a degradation rate of 0.792 mV h\(^{-1}\). In contrast, the OCV of the 1-based RCM dropped from 0.951 to 0.834 V over 120 h, for a degradation rate of 0.606 mV h\(^{-1}\), indicating more stable cell performance under the ADT condition. \( j_{0.6 \text{ V}} \) curves after ADT for 120 h (the dotted lines in Figure 3a,b) further confirmed the 1-based RCM had higher stability than the pristine and Ce salt-based RCMs. The \( j_{0.6 \text{ V}} \) of the 1-based RCM dropped from 0.951 to 0.834 V over 120 h, for a degradation rate of 0.606 mV h\(^{-1}\), indicating more stable cell performance under the ADT condition. \( j_{0.6 \text{ V}} \) curves after ADT for 120 h (the dotted lines in Figure 3a,b) further confirmed the 1-based RCM had higher stability than the pristine and Ce salt-based RCMs. The \( j_{0.6 \text{ V}} \) of the 1-based RCM after the ADT (Figure 3c) was 1.247 A cm\(^{-2}\), indicating it retained 63.5% of its initial value, while the pristine and Ce salt-based RCM retained 42.4 and 60.4% of their initial \( j_{0.6 \text{ V}} \) after the ADT, respectively. Then, the amount of fluoride ions in the exhaust water evolved from the cathode and anode during the ADT was measured. Figure 3f shows the accumulated FER

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**Figure 2.** a) Cross-sectional scanning electron microscope (SEM) image of composite membranes containing Ce complexes for proton exchange membrane fuel cell (PEMFC). b) Ion exchange capacity (IEC) and c) proton conductivity \( (\sigma_{\text{H}^+}) \) of pristine, Ce salt, and Ce complex-containing reinforced composite membranes (RCMs). d) Fluoride emission rate (FER) of the RCMs.
values calculated from the exhaust water from the anode (square) or cathode (circle) of the cell during the ADT. After 120 h of the ADT, the FER from the 1-based RCM was 1.66 and 4.03 μg cm⁻² h⁻¹ for the anode and cathode, respectively. In contrast, the pristine and Ce salt-based RCM showed ≈4 and ≈2 times higher FER values from the exhaust water than the 1-based
RCM, respectively. These results verified the significant enhancement in the durability of the membrane by the addition of the highly efficient radical scavenging Ce complex, 1. Due to the higher electrochemical redox response of the complex 1 than Ce salts toward \cdot OH radical scavenging (Figure 1f), the complex 1 in the RCM can effectively react with the in situ generated \cdot OH species before they attack the PFSA ionomer, preventing chemical degradation of the RCM. These results are consistent with the ex situ chemical degradation test shown in Figure 2d, where the complex 1-based RCM showed the lowest FER value. Moreover, because complex 1 possesses a negative charge, unlike the free Ce$^{3+}$ ion, the proton transport pathway was not blocked by radical scavengers, thereby the PEMFC did not show an overall performance drop with the addition of antioxidants.

2.3. Application of the Ce Complex Radical Scavenger in OPVs

It has been reported that organic materials which contact a ZnO interlayer can be decomposed by oxidation reactions with hydroxyl radicals, which are formed by the photocatalytic reaction on the metal oxide surface.$^{[16]}$ Therefore, we further investigated the radical-scavenging Ce-based coordination complex 1 as an antioxidant for OPVs, used as an interfacial material between the ZnO and the photoactive layer in the OPV device. The OPV device architecture is indium tin oxide (ITO)/ZnO/Ce complex 1/poly[2,6-(4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene)-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c,4,5-c'-dithiophene-4,8-dione]) (PBDB-T): 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']

Figure 4. a) Schematic diagram of the OPV device configuration. b) J–V curves of OPV device with different interlayers; ZnO and ZnO/Ce complex 1. c,d) Evolution of J–V curves of OPV device with (c) ZnO and (d) ZnO/Ce complex 1 interlayers under 1 sun exposure. Evolution of e) normalized power conversion efficiency (PCE) and f) normalized \textit{V}_{OC} of OPV devices under 1 sun exposure.
dithiophene (ITIC)/MoOₓ/Ag (Figure 4a) and the detailed fabrication conditions are provided in the Experimental Section. The J–V curves of the OPV devices are shown in Figure 4b and the parameters are summarized in Table 1. The Ce complex 1 device showed a power conversion efficiency (PCE) of 9.66% with an OCV (V_OC) of 0.91 V, a short-circuit current density (J_SC) of 16.46 mA cm⁻², and a fill factor (FF) of 64.51%. This performance was comparable to that of the control device, with a PCE of 9.68% with a V_OC of 0.91 V, a J_SC of 16.50 mA cm⁻², and an FF of 64.50%. This result indicates the introduction of the Ce complex as an interfacial layer did not significantly disturb the charge transfer between ZnO and the photoactive layer.

Furthermore, when we compared the conductivity of the interlayers by measuring J–V curves using a sandwich structure of ITO/ZnO/Ce complex 1/Ag, the ZnO/Ce complex 1 interlayer exhibited a conductivity of 3.59 × 10⁻⁶ S cm⁻¹, which is comparable to the 3.48 × 10⁻⁶ S cm⁻¹ of the ZnO interlayer (Figure S6, Supporting Information).

We studied the photo-stability of the encapsulated OPV devices including the ZnO/Ce complex 1 interlayer under 1 sun exposure and compared the results with the encapsulated control device. As shown in Figure 4c–e, the ZnO-based control device suffered fast degradation during light illumination and the PCE reached 4.78%, which corresponds to 50% of the initial performance after 36 h exposure. In contrast, the device with the ZnO/Ce complex 1 interlayer maintained the PCE relatively well, over 7% under the same degradation condition (Figure 4d,e). Changes in the photovoltaic parameters (V_OC, J_SC, and FF) of the OPV devices with ZnO and ZnO/Ce complex 1 interlayer with light soaking time are summarized in Figure 4f and Figure S7, Supporting Information, showing the stability of the device improved with the addition of radical scavenging Ce complex 1. It has been reported that the photoactive layer material, ITIC, is easily degraded by hydroxyl radicals, and these hydroxyl radicals can be generated by photocatalytic reaction, where ZnO excited by UV absorption takes an electron from the water molecules adsorbed on the oxygen defects in ZnO.[16] The photo-stability of the OPV device

Table 1. OPV performance of BHJ solar cells.

| Interlayer | V_OC [V] | J_SC [mA cm⁻²] | FF [%] | PCE [%] |
|------------|---------|----------------|-------|--------|
| ZnO        | 0.91    | 16.50          | 64.50 | 9.68   |
| ZnO after 36 h UV exposure | 0.77    | 11.38          | 53.51 | 4.69   |
| ZnO/Ce complex 1 | 0.91    | 16.46          | 64.51 | 9.66   |
| ZnO/Ce complex 1 after 36 h UV exposure | 0.88    | 15.28          | 52.75 | 7.09   |

a) V_OC: Open-circuit voltage; b) J_SC: short-circuit current density; c) FF: fill factor; d) PCE: power conversion efficiency.

Figure 5. Evolution of UV–vis absorption spectra as a function of UV exposure time. ZnO and ZnO/Ce complex 1 interlayer-based film spectra change of: a) PBDB-T:ITIC blend and b) pristine ITIC. ITIC absorption maximum evolution tracking in: c) PBDB-T:ITIC and d) pristine ITIC.
with the ZnO/Ce complex 1 interlayer is improved because the Ce complex 1 radical scavenger effectively removes hydroxyl radicals at the surface of the ZnO, thus preventing the ITIC degradation.

To further study the mechanism responsible for the improved OPV stability with the ZnO/Ce complex 1 interlayer, we prepared pristine ITIC and PBDB-T:ITIC blend films with a 10 nm thickness to explore the photocatalytic reactions which occur near the interface of the ZnO. We monitored characteristic changes in the UV–vis absorption spectra as a function of UV exposure time in a nitrogen-filled glove box. As shown in Figure 5a,c, the optical density of the absorption spectrum of the PBDB-T:ITIC film deposited on ZnO gradually decreased with increasing UV exposure time, and particularly, a peak at 700 nm which is related to ITIC absorption, remarkably decreased. In contrast, the thin active layer on the ZnO/Ce complex 1 films with a 10 nm thick interlayer was more stable and ITIC absorption was maintained at up to 80% of the initial absorbance after UV light exposure for 10 min. We performed the same UV light-soaking test with the ITIC pristine film. Figure 5b,d shows the absorbance of ≈10 nm for the thin film deposited on the ZnO/Ce complex 1 interlayer, indicating much improved stability compared with the ITIC on the ZnO interlayer. The result demonstrates that the developed Ce complex 1 is a hydroxyl radical scavenger, and can suppress the photocatalytic degradation of the organic active materials at the interface with the metal oxide interlayer and thus, help ensure the high photo-stability of OPV devices.

3. Conclusion

Overall, we demonstrated that a coordination complex of Ce could modify the hydroxyl radical scavenging activity of Ce$^{3+}$ and could be widely applied as an efficient antioxidant in energy conversion and storage devices, including PEMFC and OPV, to improve their stability. In particular, the pincer-type, electron-donating ligand dipicolinate (dipic), not only improved the radical scavenging activity of the Ce$^{3+}$ metal center, but also stabilized the radical scavengers under the device-operating conditions. To use the Ce complex radical scavenger in the PEMFC, the Ce complex was added to a reinforced composite membrane with PFSAs ionomers. The addition of the Ce complex radical scavenger did not result in an initial performance drop in the PEMFC. In contrast, the application of free Ce$^{3+}$ salt to the PEMFC resulted in an initial performance drop, by blocking proton transport pathways in the membrane. Moreover, the Ce complex improved the photo-stability of an OPV device by scavenging hydroxyl radicals generated by UV irradiation. The Ce complex was applied as an interlayer between the electron transporting layer (ZnO) and the photoactive layer (PBDB-T:ITIC). This work demonstrates the potential use of Ce-based coordination complexes as a universal radical scavenger for various electrochemical energy conversion and storage devices. Moreover, we anticipated that the further development of design strategies using ligands and Ce-based coordination complexes will enable advanced and customized radical scavengers for several energy conversion and storage devices, significantly improving device stability without initial performance loss.

4. Experimental Section

Materials and Chemicals: All chemicals and solvents were used as received without further purification. Cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.5%), pyridine-2,6-dicarboxylic acid (dipicH$_2$, 98%) were purchased from Alfa Aesar. Cerium(III) acetylacetonate hydrate (Ce(acac)$_3$·xH$_2$O, %), cerium(III) chloride heptahydrate (CeCl$_3$·7H$_2$O, 99.9%), iron(II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, >99%), calcium oxide (CaO, 99.9%), sodium hydroxide (NaOH, >98%), α-pyridin (99%), hydrogen peroxide (H$_2$O$_2$, 30 wt%), and methanol (99.9%) were purchased from Sigma-Aldrich. n-propanol (99%) was purchased from Daejung Chemical Co. Ltd. Porous PTFE, Donaldson Co., films and PFSAs, EW725, 3M, ionomer was prepared for the RCMs.

Ce Complex 1: The synthetic procedure was adopted from the previous literature.[3] In an aqueous solution containing Ce(NO$_3$)$_3$·6H$_2$O (0.868 g, 2 mmol), a methanolic suspension of dipicH$_2$ (1 g, 6.0 mmol) was added slowly. The solution was stirred for 10 min, and the pH was adjusted to 6–7 by the slow addition of CaO powder, and the mixture was further stirred for 15 min at 80 °C. Yellow precipitation was filtered through a glass frit and the yellow powder was dissolved in excess hot water. The solution was cooled down to room temperature overnight, and yellow crystals of Ce$^{3+}$ (0.91 g, 0.5 mmol, 50%) were formed overnight. IR (KBr disk): 3390 (br), 1625, 1606, 1438, 1398, 1280, 1194, 1078, 930, 765, and 665 cm$^{-1}$.

Ce Complex 2: The synthetic procedure was adopted from the previous literature.[3] In a 20 mL methanolic solution containing α-pyridin (0.630 g, 3 mmol), 3 mL of 1 m NaOH aqueous solution was added and stirred to form a yellow solution. Then 10 mL of methanolic solution of CeCl$_3$·7H$_2$O (0.372 g, 1 mmol) was added to the solution, stirred for 1 h, and kept at room temperature overnight. Solids were filtered off and the filtrate was kept in the refrigerator for one week, and brown crystals of 2 (0.803 g, 0.81 mmol, 81%) were formed. IR (KBr): 3350 (br), 1652, 1591, 1568, 1472, 1447, 1376(w), 1335, 1302(w), 1295, 1257, 1237, 1159, 1149, 1091, 1049, 1011, 1001(w), 916(w), 854(w), 842(w), 836, 758, and 694 cm$^{-1}$. Brown crystals of 2 were determined to be Na$_2$[Ce(pic)$_3$]·(pic)·H$_2$O; calc to be C 27.67, H 3.65, N 4.61; found to be C 27.43, H 3.46, N 4.35.

Ce Complex 3: The Ce complex 3, cerium(III) acetylacetonate hydrate was purchased from Sigma-Aldrich and used as received for further characterization.

XPS: XPS spectra were acquired using an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific) with a monochromatic Al Kα X-ray source (1486.6 eV).

DFT Calculation: DFT calculations of structures, energies, and frequency of Ce complexes were performed using the Gaussian 16 suite software.[17] DFT was performed at the B3LYP level of theory for light atoms using the 6-31G(d,p) basis set. For the solvation model, we used the SMD water model. The free energy ($\Delta G$) values for the Ce complexes in the oxidation states (Ce$^{3+}$ and Ce$^{4+}$) were obtained from the frequency calculations. For the standard redox potential calculations in the solution, Born–Haber cycle was utilized in this study. From the $\Delta G_{\text{Ce}^{3+}/4+}$ values, $E_{\text{Ce}^{3+}/4+}$ was determined which were referred to ferrocene by using the calculated $E_{\text{Fe}^{3+}/4+}$ value of 5.031 eV.[12]

Electrochemical Response of Ce Complexes on -OH Radical by the Fenton Reaction: The electrochemical detection of -OH radicals was adopted and slightly modified from the previous literature.[14] The Ce complex-modified SPE was used for the detection of -OH radicals. The aqueous dispersion of Ce complexes (1 mg Ce mL$^{-1}$) was sonicated for 30 min and 8 μL of the dispersion was deposited onto the working electrode of the SPEC.
The SPCE was then dried in an oven at 70 °C for 1 h before use. To generate -OH radicals, the Fenton reaction was used, where the equal volumes of aqueous 10 mM H₂O₂ and 10 mM FeSO₄ solution were mixed. Then the Ce complex-modified SPCE was put into the solution, and the interaction between the electrode and -OH radical was characterized by CV in the potential range of 0.4 to −0.6 V at a scan rate of 100 mV s⁻¹. The current changes in the SPCE were measured and referred to the presence of -OH radicals, in which the difference between the currents at the oxidation and reduction peaks were determined to redox the response of Ce complex toward -OH radicals.

Fabrication of RCMs: RCMs were fabricated by modifying the roll-to-roll process.[19] To impregnate the antioxidants in the RCM, 8.3 mL of aqueous dispersion was mixed with 10.6 mL of n-propanol and 2.32 g of PFSA ionomer. Typically, the amount of antioxidant is determined to adjust 0.5 mol% of [Ce]/[SO₃ ionomer. Typically, the amount of antioxidant is determined to adjust.

The active area of the MEA was 5 cm². The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes.

Characterization of RCMs: Cross-sectional and surface images of RCMs were obtained with field-emission SEM (FE-SEM, FEI Inspect F50, Thermo-Fisher Scientific) at an activation voltage of 10 kV. All samples were coated with a Pt layer by sputter coating. IEC was measured by an acid–base titration method. Dry RCMs were immersed in aqueous 3 M NaCl for 24 h to exchange protons with Na⁺ ions. Then, 0.01 M NaOH was used to titrate the known volume of the resulting solution to identify the displaced protons. IEC of the membranes was estimated by the following equation

\[
\text{IEC} (\text{mequiv g}^{-1}) = \frac{MV}{m}
\]

(2)

where \(M\) is the concentration of NaOH, \(V\) is the consumed volume of NaOH, and \(m\) is the weight of the dry RCM sample. Proton conductivity (\(\sigma_{\text{H}+}\)) of the RCM was determined by the electrochemical impedance spectroscopy (EIS) via measurement of the ohmic resistance of the membrane at 80 °C, RH 100%. The chemical stability of the RCM was estimated using a Fenton’s test. The fresh RCMs (1 cm²) were dried and then immersed into a 10 mL of Fenton’s solution (3 wt% H₂O₂ and 2 ppm Fe²⁺) at 80 °C for 72 h, and the solution was replaced with fresh solution every 24 h. The amount of evolved fluoride ions were analyzed by the ion-selective fluoride electrode, where the reacted Fenton’s solution was mixed with the same volume of TISAB II buffer (Thermo Fisher Scientific).

Fabrication of MEAs: The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes. The MEAs were fabricated using the following processes.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

cerium, coordination complexes, organic photovoltaics, proton exchange membrane fuel cells, radical scavengers

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