Studies on Effective Generation of Mediators Simultaneously at Both Half-Cells for VOC Degradation by Mediated Electroreduction and Mediated Electrooxidation

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ABSTRACT: Of the several electrochemical methods for pollutant degradation, the mediated electrooxidation (MEO) process is widely used. However, the MEO process utilizes only one (anodic) compartment toward pollutant degradation. To effectively utilize the full electrochemical cell, an improved electrolytic cell producing both oxidant and reductant mediators at their respective half-cells, which can be employed for treating two pollutants simultaneously, was investigated. The cathodic half-cell was studied first toward maximum \([\text{Co}^{II}(\text{CN})_6]^{3-}\) generation (21\%) from a \([\text{Co}^{III}(\text{CN})_6]^{3-}\) precursor by optimizing several experimental factors such as the electrolyte, cathode material, and orientation of the Nafion324 membrane. The anodic half-cell was optimized similarly for higher \(\text{Co}_6\text{(SO}_4\text{)}_2\) (\(\text{Co}^{III}\)) yields (41\%) from a \(\text{Co}_8\text{SO}_4\) precursor. The practical utility of the newly developed full cell setup, combining the optimized cathodic half-cell and optimized anodic half-cell, was demonstrated by electroscreening experiments with simultaneous dichloromethane removal by \(\text{Co}^{III}\) via the mediated electroreduction process and phenol removal by \(\text{Co}^{III}\) via the MEO process, showing not only utilization of the full electrochemical cell, but also degradation of two different pollutants by the same applied current that was used in the conventional cell to remove only one pollutant.

INTRODUCTION

Electrochemical mediators/electrocatalysts play a pivotal role in a variety of distinct fields, such as photoelectrocatalytic water-splitting devices, 1−3 fuel cells, 4,5 aerobic redox reactions, 5,6 amperometric sensors and biosensors, 7,8 and pollutant degradation. 9−37 Electrochemical mediators/electrocatalysts operate by catalyzing the desired electrochemical reaction by shuffling electrons between the electrode and the substrate in solution, thereby exhibiting catalytic onset at a comparatively low overpotential and, thus, improving the energy efficiency. Ideally, the redox active mediators should be efficient, long-lived, highly active, and inexpensive.

The degradation of ubiquitous pollutants by mediated electrooxidation (MEO) uses metal ion redox couples with a very high standard reduction potential (e.g., \(\text{Ag}^{II}/\text{Ag}^+\), \(\text{Ce}^{IV}/\text{Ce}^{III}\), \(\text{Mn}^{II}/\text{Mn}^{III}\)) as mediators. 21−29 The MEO is an outer-cell process in which the oxidized form of the mediator is continuously fed into a pollutant-containing scrubber column to effect the pollutant degradation, and the spent mediator is electroregenerated again at the anode of a divided/undivided cell in a closed cycle using paired electrolysis. The MEO has a wide range of applications because the continuous regeneration of the active component of the redox system in the electrochemical cell and its recirculation through the scrubber column ensure its sustainable operation. Indeed, the MEO is a United Nations Environmental Programme (UN-EP)-identified process for the ambient temperature destruction of toxic organic pollutants and waste streams, including persistent organic pollutants (POPs) and dioxins, leading to their complete mineralization to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) in a shorter duration of time. 9 Up to now, MEO-based processes have been used to successfully accomplish complete mineralization of several hazardous organic industrial wastes in water 10−13 and also for the clean-up of noxious \(\text{NO}_x\) and \(\text{SO}_2\) from flue gas mixtures. 14−17 In our laboratory, we have tested the MEO process for the last 10 years from small- to bench-scale and later to pilot-scale stages with different metal ion mediators, such as \(\text{Ce}^{IV}\), \(\text{Ag}^{II}\), \(\text{Co}^{III}\), etc., for the complete mineralization of liquid organic wastes. 10−21 destruction of noxious \(\text{NO}_x\) and \(\text{SO}_2\) gases 22−24 and \(\text{H}_2\text{S}\) odor gas, 25 and electrochemical incineration of the gas phase volatile organic compounds (VOCs) 26−29 in semibatch and continuous processes.

The cell for mediator generation in the MEO process is generally a thin-layer flow-type electrochemical reactor with anode and cathode compartments separated by a 0.15 mm thick proton conducting Nafion324 membrane. Mineral acids of high concentrations (5−10 M) are used as the electrolyte, for example, \(\text{HNO}_3\) (for \(\text{Ag}^{II}/\text{Ag}^+\), \(\text{Ce}^{IV}/\text{Ce}^{III}\)) or \(\text{H}_2\text{SO}_4\) (for \(\text{Co}^{III}/\text{Co}^{II}\)). The membrane is capable of allowing protons from the anodic to the cathodic compartment to maintain the

Received: March 24, 2017
Accepted: June 21, 2017
Published: July 13, 2017

DOI: 10.1021/acsomega.7b00352
ACS Omega 2017, 2, 3562−3571
Co3+/Co2+-based MEO system, for example, with Co(III)SO4 present in the anolyte, the Co3(SO4)2 (Co3+) mediator is generated in the anodic compartment, whereas proton reduction occurs at the cathode. During these processes, one can see that the supplied current for electrolysis is successfully utilized toward pollutant degradation by way of mediator generation only in the anodic half-cell. We believe that there exists a great scope for availing the benefit of the full electrochemical cell if the cathodic reaction is tailor-made toward the formation of a reductant mediator at the cathode in the same cell, so that both the electrogenerated mediators can be used to treat two pollutants at the same time with overall improved pollution degradation efficiencies compared to those of the conventional cell generating only one mediator for the degradation of only one pollutant via the MEO process (see Figure 1). To the best of our searching efforts, we found no published article addressing the production of two different mediators effectively in the same divided electrolytic cell in a real flow-cell operation for application toward pollutant abatement. Further, it is surprising that there has been no published report on the mediated electroreduction (MER)-based pollutant treatment in an external reactor column integrated with the cathodic compartment of a direct electrolytic cell for the regeneration of a reductant mediator, and, in a first report on this aspect, we recently studied MER of gaseous CCl4 using a Ni+ mediator30 and MER of gaseous trichloroethylene by Co+ species.31

Thus, the objective of the present work was to develop a full cell setup as outlined in Figure 1, with simultaneous generation of [Co(CN)5]4− (Co+) from [Co(CN)5]3− in the divided half-cell and Co3(SO4)2 (Co3+) from Co(III)SO4 at the anode occurring in the divided cell, and to demonstrate simultaneous degradation of two different pollutants utilizing the electrogenerated Co+ and Co3+ mediators. Cobalt precursors were chosen as model compounds due to their vast applications in basic electrochemical studies31,36,37 and paired electrolysis processes.12,17,26,19 In the first phase of the work, the cathodic half-cell was studied in detail to optimize the cathodic Co+ generation toward its higher yield. This involved estimating the quantity of Co+ produced in the cathode chamber during constant current electrolysis and investigating the influence of several experimental factors toward maximizing its yield. The effect of different electrolytes and different Co2+ precursors was studied, in addition to the effect of different metal electrodes, such as Pt, Ag, Cu, Ti, as cathodes because these metals are stable in an alkaline environment and are good for reduction reactions.38,39 The orientation of the Nafion membrane with its “+ marked” (SO3− groups exposed) side facing the anode or cathode in the divided cell was also examined in improving the Co+ yield. Changes in the H2O+ ion concentration in the electrolyzed catholyte and anolyte arising due to membrane orientation were estimated from 1H NMR chemical shifts as per the method reported by Murakhtina et al.40

Changes in the proton content of the electrolytes were also confirmed by NIR spectral measurements.35 Subsequent to the efficient generation of the Co+ mediator in the catholyte, the anodic half-cell was optimized toward maximum generation of Co3+ from Co(III)SO4 oxidation utilizing different anodes, such as Pt, mixed oxides RuO2/IrO2-coated Ti (DSA), and graphite. Following this, the optimized cathodic and anodic half-cells were integrated into a full cell to simultaneously produce Co+ and Co3+ at their maximum rate at the cathode and anode, respectively, and flow-cell experiments were conducted, in which electrogenerated Co3+ was used to dechlorinate gaseous dichloromethane (DCM) via MER in a scrubber column in a closed loop with the cathode compartment of the cell, along with Co3+ used to mineralize gaseous phenol via MEO in another scrubber column integrated with the anode chamber (electrolytes and mediators will not get exposed to the environments42). Through cyclic voltammetry, the electrocatalytic activity of Co+ toward DCM reduction and that of Co3+ toward phenol oxidation were evaluated. The degradation of DCM and phenol was monitored by gas chromatography (GC) analysis.

## RESULTS AND DISCUSSION

**Optimization of Cathodic Half-Cell toward Higher Co+ Generation from Co2+ Reduction.** In the most commonly used Co3+ (Co3(SO4)2) mediator-based MEO system with a divided cell for mediator generation, Co(III)SO4 is used as the
precursor (10 mM) in the anolyte with aqueous H2SO4 acid (5 M) as the electrolyte in both anodic and cathodic half-cells and Pt as the anode and cathode. Co3+ is generated anodically from Co3SO4 (reaction 1), whereas the hydrogen evolution reaction (HER) occurs from H2SO4 acid at the cathode (reaction 2).

At the anode:

\[ \text{Co}^{2+} \rightarrow \text{Co}^{3+} + e^- (E^{0}_\text{Co^{3+}/Co^{2+}} = 1.602 \text{ V (SCE)}) \]  

(1)

At the cathode:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) (E^{0}_{\text{H}^+/\text{H}_2}) = -0.240 \text{ V (SCE)}) \]  

(2)

In our first attempt to produce a Co+ mediator at the cathode, the same precursor salt, Co3SO4, was used in a 5 M H2SO4 catholyte, and the electrolysis was carried out. Yet, H2 was evolved and no Co+ was formed from Co3SO4. Although the HER is more facile when the proton concentration is high, it occurs at more negative potentials in solutions of low H+ ion concentration as there is a shift of \( E_{\text{H}^+/\text{H}_2} \) by −60 mV per unit increase of pH.43 With these considerations, we speculated that a highly alkaline electrolyte as a catholyte could provide the basis for Co3SO4 reduction to Co+ because by working in solutions of sufficiently high pH, the Co3SO4 reduction generating Co+ species at the cathode should occur much before H2 evolution. The results presented below validate this concept, and 10 M KOH was used as the catholyte for further work. However, Co3SO4 could not be used as the precursor for Co+ generation because of its low solubility in KOH due to the formation of a hydrated Co3(OH)2 precipitate. From a thorough literature survey, pentacyanocobalt(II) \([\text{Co}^{II}(\text{CN})_5]^{3-}\) was chosen as the appropriate precursor for Co+ \([\text{Co}^{II}(\text{CN})_5]^{3+}\) species generation (reaction 3) because \([\text{Co}^{II}(\text{CN})_5]^{3+}\) has been reported35 to be soluble in KOH and is a very strong reducing agent \((E^0\text{ for the }[\text{Co}^{II}(\text{CN})_5]^{3+}/[\text{Co}^{II}(\text{CN})_5]^{3+} \text{ couple } = -1.2 \text{ V (SCE)} )\) in 12 M KOH with a pH of 18.41

\[
\begin{align*}
[\text{Co}^{II}(\text{CN})_5]^{3+} + e^- & \xrightarrow{12 \text{ M KOH}} [\text{Co}^{I}(\text{CN})_5]^{3+} (E^{0}_{\text{Co^{+3}/Co^{+2}}} = -1.2 \text{ V (SCE)}) \\
\end{align*}
\]

(3)

Interestingly, using 10 mM \([\text{Co}^{II}(\text{CN})_5]^{3-}\) in a 10 M KOH catholyte allowed Co+ formation at the Pt cathode, and Figure 2 (dashed line) shows the amount of Co+ formed at different current densities (cd’s) as a function of electrolysis time. Figure 2 (dashed line) shows that the Co+ yield increased with the increase in the electrolyzing current; however, measurable quantities of Co+ were formed at the Pt cathode only at high cd’s (0.50 ± 0.03 mA after a 6 h electrolysis at a cd of 50 mA cm−2). To check whether the Co+ yield could be enhanced, Ag was used as the cathode in the next set of experiments. Interestingly, with the Ag cathode, the Co+ formation was significantly improved to 2.10 ± 0.11 mM after a 6 h electrolysis at 50 mA cm−2, as shown in Figure 2 (solid line).

It is important to mention here that gas evolutions, although of less intensity, were observed at both the cathode (Ag) and the anode (Pt) during electrolysis. These reactions could compete with the desired electrode reactions and hence could cause power loss and reduce the current efficiency (CE) of the mediator generation. The undesirable gas evolution reaction at the cathode in KOH can be identified25,46 as water reduction releasing hydrogen gas and hydroxide ions (reaction 4).

\[ \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (E^0 = -1.063 \text{ V (SCE)}) \]  

(4)

In addition, because the electrolytes contained dissolved oxygen, two side reactions, that is, O2 reduction to OH− (reaction 5) and/or H2O2 (HO2−) in alkaline solutions (reaction 6), could occur at the cathode in KOH as follows

At the cathode:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- (E^0 = 0.161 \text{ V (SCE)}) \]  

(5)

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- (E^0 = -0.316 \text{ V (SCE)}) \]  

(6)

At the anode, the oxidation of H2O liberates oxygen gas and proton (reaction 7)

At the anode:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- (E^0 = 0.989 \text{ V (SCE)}) \]  

(7)

The H+ ions so generated at the anode would be driven to the catholyte electrostatically and also due to the H3O+ ion concentration gradient between the anolyte (5 M H2SO4) and catholyte (10 M KOH). This facile, uninterrupted H3O+ ion transport across the Nafion membrane, arranged as suggested by its manufacturer with its "SO4−" groups exposed50,51 side facing the anode (henceforth referred to as "NO"), could drive and sustain the H2 and O2 evolution reactions at the cathode (reaction 4) and the anode (reaction 7), respectively. An additional driving force for the H2 and O2 evolution reactions was provided by the fact that the high concentration of KOH in the cathodic part could convert the exchanged H+ ions to water immediately. On the basis of these considerations, we speculate that by arranging the Nafion membrane such that its "SO4−" groups exposed" side faces the cathode (intentionally reversed, henceforth referred to as "RO"), the flow of H2O2 ions to the cathodic compartment could be diminished to some extent so that fewer protons migrate to the cathode chamber, which, in
turn, could slow down the gas evolution reactions, consequently leading to an improved Co substance conversion efficiency. Indeed, electrolysis data collected from the above cell arrangement with the membrane in RO showed higher quantities of Co⁺ (2.64 ± 0.13 mM) compared with the smaller quantities of Co⁺ (2.10 ± 0.11 mM) with the membrane in NO, as shown in Figure 3A, validating our above hypothesis. Interestingly, matching with the above observation, changes in the H₃O⁺ ion concentration in the electrolyzed solutions of the cathode and anode, arising due to the membrane orientation, displayed a similar behavior, as shown below, and supported our suggestion further.

Changes in the hydrogen ion concentration in electrolyzed catholyte and anolyte solutions with the Na⁺ containing a 10 M KOH catholyte at the Ag cathode with the Nafton membrane in different arrangements, NO and RO. (B) Concentration of Co⁺ electrogenerated from 10 mM [Co⁰(CN)₅]³⁻ containing a 10 M KOH catholyte with the Nafton membrane in RO with different cathodes: (A) Ag; (B) Ti; (C) Cu. Current density = 50 mA cm⁻²; electrolyte solution flow rate = 100 mL min⁻¹.

Figure 3. (A) Concentration of Co⁺ electrogenerated from 10 mM [Co⁰(CN)₅]³⁻ containing a 10 M KOH catholyte at the Ag cathode with the Nafton membrane in different arrangements, NO and RO. (B) Concentration of Co⁺ electrogenerated from 10 mM [Co⁰(CN)₅]³⁻ containing a 10 M KOH catholyte with the Nafton membrane in RO with different cathodes: (A) Ag; (B) Ti; (C) Cu. Current density = 50 mA cm⁻²; electrolyte solution flow rate = 100 mL min⁻¹.

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Changes in the hydrogen ion concentration in electrolyzed catholyte and anolyte solutions with the Nafton membrane in two different orientations were obtained from changes in ¹H NMR chemical shifts of H₂O⁺ ions, as per the method reported by Murakhchina et al., showing that the ¹H NMR chemical shift values are linearly correlated with the acid concentration. The ¹H NMR traces recorded for catholyte and anolyte solutions before and after electrolysis with the Nafton membrane in two different orientations are shown in Figure S1. The chemical shift values (δ), corrected for the solvent water (δ_H₂O = 4.778 ppm), for different systems are summarized in Table 1. Change in the ¹H NMR chemical shift (Δδ) along with change in the hydrogen ion concentration (Δ[H⁺]), calculated from (Δδ), are also included in Table 1. One can see from the Δ[H⁺] results that there was a small increase in the H₃O⁺ ion concentration after electrolysis in the catholyte chamber with the membrane in RO (Δ[H⁺] = +10.87 mM), compared with a large build-up of H₂O⁺ after electrolysis in the catholyte, when the membrane was in NO (Δ[H⁺] = +57.97 mM), as expected. Expanding further, the accumulated smaller proton concentration with the membrane in RO highlighted here clearly indicates reduced flow of H₂O⁺ from the anolyte to the catholyte, resulting in enhanced mediator production, as proposed earlier. For the accompanying proton concentration changes in anolytes, see Table 1. In addition to ¹H NMR studies, the NIR spectroscopic technique was used for the identification of H₂O⁺ ions (as H₂O in KOH) because of its specificity to the H₂O concentration. The NIR spectra obtained by subtracting spectral outputs before and after electrolysis, monitored in the cathode compartment, for the membrane in two different orientations are shown in Figure S2. The absorption peaks (Figure S2) close to the reported −O−H stretching and bending vibrations (1456 and 1900 nm) indicate the presence −O−H of hydronium ions, for the case of the membrane in NO, suggesting facile migration of H₂O⁺ ions to the cathodic compartment. In contrast, diminished peak intensities (low H⁺ ion concentration) were found for the membrane in RO, showing reduced migration of H₂O⁺ ions into the cathode chamber.

It is important to realize that the electrolytic cell with the membrane in NO showed a cell voltage of 4.46 V, when operated at a 50 mA cm⁻² current density. However, for the cell with the membrane in RO, the cell voltage was higher at 4.92 V, under similar operating conditions. Such an increase of the cell voltage by 460 mV accompanying the membrane in RO could be a manifestation of an increased ohmic drop across the membrane due to increased membrane resistance arising due to decreased proton conduction from the anolyte to catholyte. The Nafton324 resistance was analyzed by electrochemical impedance spectroscopy under the galvanostatic mode, and the results are presented in Figure S3. Through the Nyquist diagram, the Nafton324 resistance at NO was found to be 88.9 Ω cm⁻² (Figure S3, curve a), which is lower than 233.2 Ω cm⁻² for Nafton324 in RO, clearly accounting for the proton diminution to the catholyte.

**Studies with Different Cathode Electrode Materials for Co⁺ Generation.** As the nature of the electrode material greatly influences the rates of redox reactions and often changes the reaction path, product distribution, and the product yield in several cases, we tested for the higher yields of Co⁺ with various cathodes, such as, Ti and Cu. In all of these measurements, the Nafton membrane was arranged in RO. Figure 3B shows that Ag appeared to be the best cathode among the metals investigated in generating higher quantities of Co⁺, with the Cu cathode showing the least effect. Their ability increased in the order

\[ Ag > Ti > Cu \]  

(8)

The half-cell potentials (SCE) measured for different cathodes were found to be −1.24 V for Ag, −1.05 V for Ti, and −0.28 V for Cu. Because of the fact that the Cu cathode has a more positive potential than that required for reducing the
Co$_3^+$ concentration is not due to the crossover of cobalt ions. Further, UV−visible analysis confirms that the absence of migration of cobalt ions to the cathodic half-cell during the electrolysis in NO (Figure S4, curve a) evidences that the decrease in the analysis concentration of Co$_3^+$ could be less than that by the Ag and Pt cathodes, as observed experimentally. However, further detailed fundamental electrochemical studies are needed to understand the electron transfer kinetics and mechanism, and this is not the focus of the present work. As Ag was found to generate higher quantities of the Co$_3^+$ mediator ion, it was used as the cathode of the optimized cathodic half-cell in the integrated cell setup.

**Optimization of Anodic Half-Cell toward Higher Co$_3^+$ Yield from Co$_5^+$ Oxidation.** Of the four parameters that directly affect the Co$_3^+$ formation at the anode, the effect of only two parameters, that is, membrane orientation and type of anode material, was examined here because the other two influencing factors, the electrolyte (H$_2$SO$_4$) and the Co$^{2+}$ precursor (Co$_3$IISO$_4$), were used as standard ones in several Co$_3^+$-based MEO studies.$^{17,26}$

Thus, the anodic half-cell (10 mM Co$_3$IISO$_4$ in a $5\ M$ H$_2$SO$_4$ anolyte with a Pt anode) was studied for Co$_3^+$ generation with Pt, it was preferred and used as the anode material, was examined here because the other two influencing factors, the electrolyte (H$_2$SO$_4$) and the Co$^{2+}$ precursor (Co$_3$IISO$_4$), were used as standard ones in several Co$_3^+$-based MEO studies.$^{17,26}$

| Table 1. $^1$H NMR Chemical Shift, $\delta$ (ppm), Corrected for the Solvent Water ($\Delta$H$_{2O}$ = 4.778 ppm), Change in Chemical Shift $\Delta\delta$ (ppm), and Change in Hydrogen Ion Concentration $\Delta$H$_3O^+$ (mM) for the Catholyte and Anolyte before and after Electrolysis in an Electrolytic Cell$^a$ with the Nafion Membrane Arranged in NO and RO during Optimization of the Cathodic Half-Cell |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| sample                                     | $\delta$ (ppm) | before electrolysis | after electrolysis | $\Delta$ (ppm) | $\Delta$H$_3O^+$ ($\mu$M) |
| catholyte                                  | $-0.077$       | $-0.061$         | $+0.016$         | $+57.97$       | $+0.003$         | $+10.87$        |
| anolyte                                    | $2.194$        | $2.076$          | $-0.118$         | $-427.54$      | $-0.076$         | $-0.075$        | $+0.001$        | $+3.62$        |

$^a$Divided electrolytic cell with the cathodic half-cell comprising 10 mM [Co$_3$(CN)$_5$]$^{3-}$ catholyte in 10 M KOH with a Ag cathode, and anodic half-cell comprising 10 mM Co$I$ISO$_4$ anolyte in 5 M H$_2$SO$_4$ with a Pt anode; current density = 50 mA cm$^{-2}$, electrolysis time = 4 h. $^b$$\Delta$H$_3O^+$ (in mM) was calculated from $\Delta\delta$ (in ppm) using a value 0.276 ppm M$^{-1}$ from the $\delta$−$\varepsilon$ plot in Figure 5 of ref 40. $^c$Electrolysis carried out under the same conditions as in footnote (a) but without Co compounds in the electrolytes.

Figure 4. (A) Concentration of Co$^{3+}$ electrogenerated from 10 mM Co$_3$IISO$_4$ containing a 5 M H$_2$SO$_4$ anolyte with a Pt anode and the Nafion membrane in NO and RO arrangements. (B) Concentration of Co$^{3+}$ electrogenerated from 10 mM Co$_3$IISO$_4$ containing a 5 M H$_2$SO$_4$ anolyte with the Nafion membrane in RO with different anodes: (A) Pt; (B) DSA; (C) graphite. Current density = 50 mA cm$^{-2}$.
as the anode of the optimized anodic half-cell in the integrated cell setup.

**Optimized Full Cell Setup.** Finally, the optimized cathodic half-cell (10 mM \([\text{Co}^{II}(\text{CN})_{5}]^{3-}\) in 10 M KOH with a Ag cathode) and the optimized anodic half-cell (10 mM \(\text{Co}^{II}\text{SO}_4\) in a 5 M \(\text{H}_2\text{SO}_4\) anolyte with a Pt anode) were combined into a full cell setup with the Nafion membrane in the cell arranged in RO. Figure 5 illustrates the concentrations of Co\(^+\) and Co\(^{3+}\) simultaneously produced at their maximum rate at the cathode and anode, respectively, during continuous electrolysis in such a combined cell.

The CE for the generation of reactive cobalt species was estimated. The CE for both Co\(^+\) and Co\(^{3+}\) formation decreased with the electrolysis time during a 6 h electrolysis, as reported for the formation of peroxomonomophosphate at the BDD anode (1%) and ethane and ethene formation at the Ag cathode (15%). The CE values for the formation of both Co\(^+\) and Co\(^{3+}\) were higher, 21.5% (at 120 min), than around 1% reported for peroxomonomophosphate formation (Figure 3 of ref 49). The energy consumption, calculated as energy spent (kWh) for 1 kg mediator production, showed: for the generation of 1 kg of Co\(^+\) at the cathode, more energy was required (ca. 154 kWh at 4 h) compared to 121 kWh for 1 kg of Co\(^{3+}\) at the anode under the same experimental conditions.

**Implications of the Present Work in Pollutant Destruction: Coupled MER and MEO Processes for Organic Pollutant Destruction in a Continuous Process.** Flow-cell experiments involving mediator generation coupled with a scrubber column were conducted for pollutant degradation using the optimized full cell setup described above. The experiments involved simultaneous generation of Co\(^+\) at Ag and Co\(^{3+}\) at Pt for a certain amount of time, following which 75 ppm of gaseous DCM to the cathode scrubber and 65 ppm of phenol to the anode scrubber were injected at a gas flow rate of 0.5 L min\(^{-1}\), so that DCM was subjected to degradation by Co\(^+\) via the MER process and phenol was subjected to simultaneous degradation by Co\(^{3+}\) via the MEO process, with the electrolytic cell continuously working for the sustained regeneration of mediator ions Co\(^+\) and Co\(^{3+}\). During the entire course of electrolysis, concentrations of Co\(^+\) and Co\(^{3+}\) were measured continuously.

The electrogenerated Co\(^+\) mediator shows 99.25% removal of DCM (75 ppm) gas in 5 min, which was decreased to 70%, and then maintained up to 1 h studied (Figure 6, curve b). It should be noted that 40–50% of gaseous DCM was removed in 5 min, which dropped to 0% removal efficiency in 15 min when the solution was devoid of the electrogenerated mediator (Figure 6, curve a) or absorption, confirming that the DCM removal followed the MER process. This is illustrated in Figure 6 (inset), which shows the concentration of Co\(^+\) in the catholyte as a function of electrolysis time. When DCM (75 ppm) was injected to the catholyte scrubber, it was spontaneously reduced by the available electrogenerated Co\(^+\) species with a sudden dip in the Co\(^+\) concentration from 1.8 to 0.3 mM, which indicates that the MER process has occurred and the electrogenerated Co\(^+\) has degraded the DCM. To evaluate the MER of DCM by Co\(^+\), CV experiments were carried out and presented in Figure S5. DCM was not directly reduced on Ag (curve b). Indeed, a strong adsorption of DCM species with a sudden dip in the Co\(^+\) reduction current (curve d) due to mediated reduction of DCM by the electrogenerated Co\(^+\), as shown in Scheme 1. To identify the reduction products, the electrolyte solution (before and after DCM removal) was subjected to ATR–FTIR, and the subtracted ATR–FTIR spectrum is depicted in Figure S6, wherein the resultant spectrum is well matched with ethanol stretching frequencies C–O and OH and with the standard ethanol spectrum from the instrument’s library. In addition, the electrochemical reduction of DCM at the metal electrodes in aprotic solvents...
ended up with higher molecular weight hydrocarbons such as propene, ethylene, butane, etc., via carbene formation. It is noteworthy that ethanol was identified as the major product during the ClC₂ reduction via MER in a highly alkaline medium, and all of these data highly support our results that the formed product is ethanol (see Scheme 1).

In the case of gaseous phenol (65 ppm) oxidation by the electrogenerated Co³⁺, the system showed 100% phenol removal immediately and lasted for 1 h and beyond (Figure 7, curve b), which is additionally evidenced by the associated ppm of phenol and 10 mM CoIISO₄ (Figure S7, curve d)) showed that the Co³⁺ electrogenerated from 10 mM CoIISO₄ in 5 M H₂SO₄ in the alkaline medium, and all of these data highly support our results that the formed product is ethanol (see Scheme 1).

The voltammogram for the corresponding system (Pt anode at −1 scan rate in a 5 M H₂SO₄ solution containing 50 ow rate = 2 L min⁻¹; feed gas concentration = 65 ppm; gas flow rate = 0.5 L min⁻¹. Inset figure shows Co⁺ concentration variation when injecting phenol to the scrubber column.

Co³⁺ concentration variation, as shown in Figure 7 (inset). Upon injecting 65 ppm phenol, the Co³⁺ concentration decreased from 3.2 to 1.5 mM because most of the available Co³⁺ ions were used up by the added phenol. The mechanism concerning phenol oxidation by Co³⁺ is depicted in Scheme 2. The voltammogram for the corresponding system (Pt anode at a 100 mV s⁻¹ scan rate in a 5 M H₂SO₄ solution containing 50 ppm of phenol and 10 mM Co²⁺SO₄ (Figure S7c, curve d)) showed that the Co⁴⁺ electrogenerated from Co²⁺SO₄ could effectively mediate phenol oxidation. On the basis of our previous experience on solution-phase phenol oxidation, a separate study was carried out using a CO₂ analyzer to understand the product that was formed in phenol oxidation. Figure S8 (curve a) illustrates an increase in the CO₂ concentration (ppm) from 0 to 450 ppm instantaneously, which is maintained for a while followed by a little increase after 1.5 h, confirming that the final product is CO₂ (see Scheme 2). It is noteworthy that the solution-phase phenol oxidation by electrogenerated Ce⁴⁺ and Ag²⁺ resulted in CO₂ as the final product. The reason for the mismatch in the exit CO₂ concentration and electrogenerated mediator Co³⁺ could be: slow mediation kinetics at room temperature; higher number of electrons (28) required for its complete mineralization; the reaction proceeding through several slowly degrading intermediates, etc.

Table 2 summarizes the generation efficiencies of both Co⁺ and Co³⁺ mediators and the accompanying degradation efficiencies of both DCM and phenol, achieved simultaneously from the above improved cell setup. The table also includes the generation efficiency for the Co³⁺ mediator and the corresponding phenol degradation efficiency from the conventional cell used in the MEO process (Figure 1). It is clear that with 25 mA/cm² cd used for electrolysis, 35% Co³⁺ alone was formed over a period of 200 min in the conventional cell. However, interestingly, by integrating the active anolyte chamber with an active catholyte chamber, as in the improved cell setup, 23% of the Co³⁺ mediator was produced at the cathode in addition to the 35% Co³⁺ at the anode with the same cd of 25 mA/cm². This additional benefit is a key factor that indicates that unlike the conventional cell, the improved electrolytic cell system utilizes the maximum spent current for electrolysis (less that the quantity used up by side reactions) toward pollutant degradation because this later cell provides two mediators to treat two pollutants simultaneously. Table 2 also indicates that the improved electrolytic cell ensured degradation of more than one pollutant (DCM and phenol) with a removal efficiency of 70% for DCM and 100% for phenol, which is a significant improvement over the conventional cell used to generate only one mediator, which permitted removal of one pollutant (phenol) by MEO with 100% degradation efficiency.

**CONCLUSIONS**

In summary, we have demonstrated that two mediators can be generated in a single divided electrochemical cell by the same applied current that is used to generate one mediator in a conventional cell. We have shown that it is possible to generate high concentrations of scalable mediators Co³⁺ (35%) and Co⁺ (23%) by employing a highly acidic medium (5 M in anodic half-cell) and a basic medium (10 M in cathodic half-cell), suitable mediator precursors (CoIISO₄ in the anodic half-cell and [Co⁴⁺(CN)₆]³⁻ in the cathodic half-cell), suitable catalytic electrodes, along with the effect of proton transfer by the Nafion membrane separator in a suitable configuration. Further, the two electrochemically generated mediators were applied successfully to remove two different gaseous pollutants, DCM (70%) and phenol (100%), simultaneously via the MER and MEO processes. Pertinent issues, such as screening of active mediators, especially for the MER process, their stability under reaction conditions, the effect of the electrode and electrolyte on the mediator generation reaction and mediator yields of both the cathodic and anodic processes, and the mutual effect...
Table 2. Comparison of Performance of the Improved Electrolytic Cell Setup with the Conventional Cell Used in the MEO Process

|                          | conventional cell used in MEO process | improved electrolytic cell setup |
|--------------------------|--------------------------------------|---------------------------------|
|                          | anolyte                              | catholyte                       | anolyte                          | catholyte                       |
| mediator conversion efficiency at 200 min after electrolysis | 35% (Co\(^{2+}\) generation)         | 35% (Co\(^{2+}\) generation)     | 100% (phenol mineralization)      | 100% (phenol mineralization)     |
| pollutant degradation efficiency | 100% (phenol mineralization)          | 23% (Co\(^{3+}\) generation)    | 70% (DCM degradation)             |                                |

“Improved electrolytic cell setup: A divided electrolytic cell with 10 mM \([\text{Co}^{II}(\text{CN})_5]^3-\) in a 10 M KOH catholyte, 10 mM Co\(^{3+}\)SO\(_4\) in a 5 M H\(_2\)SO\(_4\) anolyte, Ag cathode, Pt anode, Nafion membrane in RO, current density = 25 mA cm\(^{-2}\). \(^9\)Conventional cell used in the MEO process: A divided electrolytic cell with a 5 M H\(_2\)SO\(_4\) catholyte, 10 mM Co\(^{3+}\)SO\(_4\) in a 5 M H\(_2\)SO\(_4\) anolyte, Ag cathode, Pt anode, Nafion membrane in RO, current density = 25 mA cm\(^{-2}\). \(^9\)In the conventional cell used in the MEO process, the cathodic reaction at the Ag cathode in a 5 M H\(_2\)SO\(_4\) catholyte is H\(_2\) gas evolution (see Figure 1)."

of the cathode on the Co\(^{3+}\) yield at the anode and vice versa, are to be investigated to promote the present process to a near-real application level.

**Experimental Section**

Preparation of Cobalt Cyanide Complex. The cobalt cyanide complex \([(\text{Co}^{II}(\text{CN})_5)]_3\text{K}_2\) was synthesized as reported previously. \(^53\) Briefly, 161.3 g of potassium cyanide dissolved in 150 mL of water was added to a cooled 160 mL solution of 120 g of Co\(^{3+}(\text{NO}_3)\) under a nitrogen atmosphere (\(~6.2\) cyanides per cobalt) and then an equal volume of chilled alcohol was added, and the resulting mixture was slowly chilled until a mass of thin violet platelets appeared. The obtained cobalt cyanide complex sample was filtered rapidly and washed with cold alcohol and then dried in a vacuum desiccator and stored in an air-tight brown bottle. *Caution! Potassium cyanide is highly toxic; proper care must be taken during handling.*

Electrolytic Cell Setup. The electrolytic flow cell used for the simultaneous generation of Co\(^{2+}\) at the cathode and Co\(^{3+}\) at the anode was of a plate-and-frame type, with a narrow gap and divided configuration. A 0.2 L solution of Co\(^{3+}\)SO\(_4\) (10 mM) in 5 M KOH were placed in separate anolyte and catholyte tanks, respectively. The anolyte and catholyte solutions were continuously circulated through the anode and cathode compartments of the electrochemical cell at constant flow rates (100 mL min\(^{-1}\)) using peristaltic pumps (Masterflex - L/S, model No. 7524-45, Cole Parmer Instrument Company) through a narrow gap of a divided cell (divided by the Nafion\(^{42}\)324 membrane). The active Co\(^{2+}\) and Co\(^{3+}\) mediators were generated galvanostatically by applying different constant current densities between 10 and 50 mA cm\(^{-2}\) using a DC power supply (Korea Switching Instruments). The effective surface area of each electrode exposed to the solution was around 600 mV, became increasingly positive with the increase in the Co\(^{3+}\) concentration, was reverted back to its initial value measured before electrolysis, \(-170\) mV. From the volume of Fe\(^{3+}\) consumed, the concentration of Co\(^{2+}\) was calculated. The concentrations were reproducible to within \(\pm 5\%\).

In a similar manner, the Co\(^{3+}\) concentration from the anode compartment was obtained by titration with Fe\(^{3+}\)\(\text{SO}_4\) \((1 \text{ mM})\). Here, the initial ORP of the Co\(^{3+}\)-containing solution, which was around 600 mV, became increasingly positive with the increase in the Co\(^{3+}\) concentration. The concentration of Co\(^{3+}\) was calculated from the Fe\(^{3+}\)\(\text{SO}_4\) titrant volume.

Analyses. The catholyte and the anolyte samples from the electrolytic cell were analyzed for their proton content, before and after electrolysis, by \(^{1}\)H NMR and NIR spectroscopy. The NMR analysis of the electrolyte samples was done using a high-resolution NMR spectrometer (400 MHz, FT-NMR, Bruker, model: AVANCE 400, Germany) without dilution. In all of the instrumental techniques, a similar sampling procedure and analysis time was maintained. For NIR measurements, 3 mL of the sample solution was placed in a rotating cup (150 mm diameter) with a Au lid covered, and the measurements were carried out in the reflectance mode in a monochromator NIR instrument between 680 and 2500 nm at a 1 nm interval (Spectra Star, model: RTW-2240, Unity Scientific). The solution-phase products were analyzed by an attenuated total reflectance–FTIR (ATR–FTIR, Thermo scientific, Nicolet iS5) using a 2 \(\mu\)L drop of the reaction sample on the diamond prism.

The removal efficiency was monitored by GC analysis using gas samples (0.5 \(\mu\)L) that were withdrawn via a gas syringe...
(model 10R-GP-GT) from the exit gas of the scrubber column after phenol oxidation or DCM reduction and were analyzed by GC using an HP 6890. A porapak Q column (length 1.8 m × 2.1 mm diameter with 80–100 molecular sieve mesh made by stainless steel tubing) was used for gas chromatographic separations (Sigma-Aldrich). The GC oven temperature was set at 200 °C, and the thermal conductivity detector temperature was fixed at 250 °C. Helium was used as a carrier at a flow rate of 2 mL min⁻¹. The migration of cobalt ions during electrolisis from the anodic half-cell to the cathodic half-cell through Nafion 324 was primarily analyzed by UV-visible spectroscopy using a Scinco s-3100 spectrophotometer.

Cyclic voltammetry experiments were carried out in a glass cell furnished with two compartments separated by a glass membrane for working and counter electrodes. A platinum mesh and a dip-type Ag/AgCl electrode were used as counter and reference electrodes, respectively. Measurements were done with a PARC VersaSTAT 3 instrument. A tailor-made Nafion membrane divided cell was used for the impedance studies by using the same PARC VersaSTAT 3 instrument. The galvanostatic mode with an applied current of 1 mA (vs OCP) using a two-electrode configuration was used with Pt as the counter and working electrodes (1 cm distance), respectively, with the frequency range between 10 kHz and 0.01 Hz.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00352.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the National Research Foundation of Korea (NRF) funded by Ministry of Engineering Science and Technology (MEST) from the Korean government (Grant No. 2017R1A2A1A05001484).

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