

## Accepted Manuscript

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PII: S1226-086X(18)30095-9  
DOI: <https://doi.org/10.1016/j.jiec.2018.02.025>  
Reference: JIEC 3885

To appear in:

Received date: 27-12-2017  
Revised date: 5-2-2018  
Accepted date: 10-2-2018

Please cite this article as: G.Muthuraman, A.G.Ramu, Y.H.Cho, E.J.McAdam, I.S.Moon, Sustainable degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced electron mediator within electro-scrubbing, Journal of Industrial and Engineering Chemistry <https://doi.org/10.1016/j.jiec.2018.02.025>

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## Sustainable degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced electron mediator within electro-scrubbing

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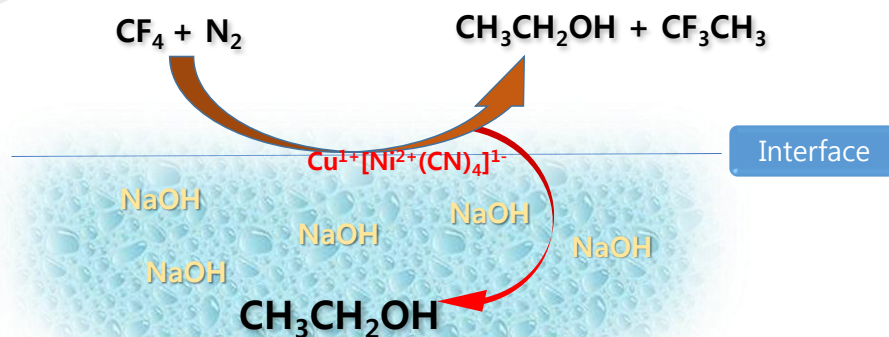
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### Graphical Abstract



**Synopsis:** Ethanol generation was established during the degradation of  $\text{CF}_4$  by mediated electrocatalytic reduction using electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  at electro-scrubbing process.

### Highlights

- A  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  complex was established for carbon tetrachloride degradation to non-corrosive useful product
- ORP and ESR results demonstrated  $\text{Cu}^{1+}$  formation at cathodic half-cell during electrolysis
- Mass transfer analysis identifies rate limiting behavior and routes to optimization
- Ethanol found to be a main product in the degradation of  $\text{CF}_4$  by MER at electro-scrubbing

### Abstract

The degradation of  $\text{CF}_4$  gas using existing technologies produces other types of greenhouse gas ( $\text{CO}_2$ ) and corrosive side products. The main aim of this study is to degrade  $\text{CF}_4$  gas at room temperature into useful products without producing corrosive side products by mediated electrochemical reduction (MER) process using an electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  mediator. Initial studies on the electrolytic reduction of the hetero-bimetallic complex in catholyte solution at anodized Ti cathode was monitored by oxidation/reduction potential (ORP) variation whether the  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  was reduced in the  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  and confirmed by electron spin resonance (ESR) spectroscopy the  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  formation. The concentration variation of  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  during  $\text{CF}_4$  injection demonstrated the

degradation of  $\text{CF}_4$  followed the MER by electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$ . Maximum removal efficiency of  $\text{CF}_4$  using electroscrubbing process was 96% at room temperature. Through the variation in gas phase parameters, the gas phase mass transfer coefficient was calculated that can facilitate scale up the developed process. Fourier transform infrared spectroscopy analysis in both the gas and solution phases showed that  $\text{CH}_3\text{CH}_2\text{OH}$  was the main product that formed during the removal of  $\text{CF}_4$  by electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  at electroscrubber along with a small amount of  $\text{CF}_3\text{CH}_3$  intermediate. Importantly, this mechanism also avoided formation of the corrosive product HF.

Keywords: Hetero-bimetal, MER,  $\text{CF}_4$  degradation; Ethanol formation

## 1. Introduction

Both etching and cleaning steps in semiconductor manufacturing make use of perfluoro gases, such as  $\text{CF}_4$ ,  $\text{NF}_3$  and  $\text{SF}_6$ , which possess high global warming potential (GWP) [1]. Consequently, growth in electronic equipment demand is driving considerable increase in GWP through the fugitive release of perfluoro gases into the environment. Of particular concern is  $\text{CF}_4$  which has 6500 time GWP of  $\text{CO}_2$  [2]. However, there are currently only a limited number of abatement technologies for perfluoro gases, which constitutes an extremely challenging separation. The two primary existing technologies are combustion and plasma arc [3-6]. Whilst the plasma etching technique could potentially be used in the electronic manufacturing industries, plasma will not typically achieve complete perfluoro gas degradation which results in formation of byproducts, notably another greenhouse gas,  $\text{CO}_2$ , and its derivatives ( $\text{COF}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ), with HF depending on the carrier gas [7-10]. Catalytic

combustion has also attracted considerable interest [11,12], particularly hydrolytic combustion because of its lower Gibbs free energy ( $-150$  kJ/mol). Unfortunately, one of the final products obtained is highly corrosive HF, as shown in reaction 1, which leads to catalyst deactivation [13]. Also, another product in the catalytic combustion in the  $\text{CF}_4$  decomposition process is  $\text{CO}_2$ , thereby further exacerbating greenhouse gas production.



The degradation of chloro fluoro carbons (CFCs) to mostly non-fluoro compounds has been achieved by electrochemical technique at room temperature without producing final products that contribute to greenhouse effects [14-16]. Copper supported gas diffusion electrode resulted in methane in degradation of  $\text{CClF}_3$  (CFC-13), and on Ag-supported gas diffusion electrode to form  $\text{CHF}_3$  [14]. The degradation of many CFCs have been performed in solution phase especially through direct electrochemical reduction on different metal electrodes in acetonitrile [17] and DMF [18] to produce,  $\text{CF}_2\text{CF}_2$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_3\text{F}$ ,  $\text{CF}_2\text{CFCl}$ , and  $\text{CHCF}_3$ , as the main products, which are used as raw materials in the production of polymers and refrigerants. A methanol/water solvent mixture was also demonstrated to degrade CFC-11 and CFC-113 using a Pb cathode with a Pd containing gas diffusion anode by constant potential electrolysis, where complete or partially dehalogenated products were achieved depending on the Pd contents [19]. To improve understanding, fundamental electrochemical studies were performed on selective site-specific PFC compounds, which showed that the reduction reaction follows a radical reaction with the formation of a carbanion with subsequent oligomeric products, such as  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CH}_4$  from  $\text{CF}_4$  etc [20]. Most electrochemical studies on CFC degradation were performed in non-aqueous media or a combination of non-aqueous and aqueous solvents using electrochemical analyzer such as CV or constant potential electrolysis;

none were performed in only aqueous medium and a constant current electrolysis in the CFCs or CF<sub>4</sub> degradation process. Recently, CF<sub>4</sub> removal was reported using a mediated electrochemical reduction (MER) in aqueous KOH medium at room temperature by the electrochemically generated mediator Co<sup>1+</sup> in an electro-scrubbing process [21]. Though, the main focus was development of room temperature removal of CF<sub>4</sub> by electroscrubbing (for the first time), the product found in the Co<sup>1+</sup> MER of CF<sub>4</sub> were HF and ethanol [21]. The HF formation not only constitutes an environmental concern but may also reduce the pH of the electrolyte in continuous electro-scrubbing process, which will inactivate mediator generation, subsequently limiting CF<sub>4</sub> removal. Consequently, provided HF formation can be avoided, sustained CF<sub>4</sub> degradation could be achieved, coupled with the generation of ethanol that could be conceived as a sustainable high-value end product. One alternative could be utilization of a binary metal complex or bimetallic complex in the CF<sub>4</sub> degradation process. Note that to minimize catalyst deactivation in catalytic combustion process, a binary metal catalyst was attempted to degrade CF<sub>4</sub> by hydrolytic combustion process, with the idea of C-F bond breaking at the Lewis-acid catalysts to form metal fluorides, which was hydrolyzed, and made possible the assessment of various bimetal combinations. The study found that Ga-Al and Ni-Al oxide catalysts were stable from HF deactivation [22-24]. In another study, the CF<sub>4</sub> was converted to CO<sub>2</sub> with minimal deactivation (by HF formation) of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts by the addition of Zn, Ni, Mg, Sr, and Ba metals [7]. A stable catalyst was achieved in catalyst combustion process using Ce/Al<sub>2</sub>O<sub>3</sub> binary catalyst but that was not effective in the removal of CF<sub>4</sub> [24].

In the present investigation, it is asserted that the hetero-bimetallic complex Cu<sup>2+</sup>[Ni<sup>2+</sup>(CN)<sub>4</sub>] can be used as a mediator precursor in the degradation of CF<sub>4</sub> gas to form a

useful end product and without the production of harmful sideproducts like HF. A constant current method was used to generate low valent active mediator generation in 10 M KOH medium at cathodic half-cell in a divided electrolytic cell to generate a low valent active mediator. An anodized Ti or TiO<sub>2</sub> cathode was used for the electrolytic reduction of Cu<sup>2+</sup>[Ni<sup>2+</sup>(CN)<sub>4</sub>] in 10 M KOH. The oxidation/reduction potential (ORP) of Cu<sup>2+</sup> and Ni<sup>2+</sup> in a dissolved electrolyzed solution during electrolysis were taken as an indication and quantification by a potentiometric titration separately for the formation of a low oxidation state active mediator. In addition, electron spin resonance (ESR) spectroscopy was used to support the differentiation of Cu<sup>2+</sup> or Ni<sup>2+</sup> reduction in an electrolyzed solution. CF<sub>4</sub> degradation was carried out within an electro-scrubber, where CF<sub>4</sub> was fed continuously at a controlled rate and concentration through the bottom of the scrubber and the spent hetero-bimetallic complex was then sent to a cathodic half-cell to generate a low oxidation state active mediator. The CF<sub>4</sub> removal efficiencies were monitored using online Fourier transform infrared (FTIR). Solution phase and gas phase analyses were conducted to determine the final product.

## 2. Materials and Methods

### 2.1 Preparation of mediator precursor.

The hetero-bimetallic Cu<sup>2+</sup>[Ni<sup>2+</sup>(CN)<sub>4</sub>] was prepared using the literature procedure [25]. In brief, Cu<sup>2+</sup>(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and [Ni<sup>2+</sup>(CN)<sub>4</sub>]<sup>2-</sup> were added to 200 ml of water at a Cu<sup>2+</sup> to Ni<sup>2+</sup> mole ratio of 1:4. A light blue precipitate formed slowly with constant stirring, which was separated by filtration, washed several times with water and dried in a desiccator prior to use. [Ni<sup>2+</sup>(CN)<sub>4</sub>]<sup>2-</sup> was prepared using the existing literature procedure [26]. Briefly, Ni<sup>2+</sup>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was taken at a 1:4 mole ratio (Ni<sup>2+</sup> to cyanide) to KCN, which was already

dissolved in 200 ml cooled water (extreme care was taken when handling the KCN during complex preparation because it is highly dangerous to humans). To this reaction solution, an equal volume of chilled alcohol was then added. The resulting thin orange platelets were filtered rapidly, washed with cold alcohol, recrystallized in ethanol, dried in a vacuum desiccator, and stored in an air-tight brown bottle.

## ***2.2 Setup and procedure for mediator generation and degradation.***

A divided flow-through electrolytic cell was used, as in a previous publication [21], under suitable additional conditions (Fig.1). Briefly, a 4 cm<sup>2</sup> working electrode area capacity thin layer plate and frame divided cell (divided with Nafion324) was connected to the catholyte (200 ml of mediator precursor in 10 M KOH) and anolyte (200 ml of 5 M H<sub>2</sub>SO<sub>4</sub>) glass tanks through polycarbon tubing to allow the anolyte and catholyte to circulate (using peristaltic pumps) through the respective anode and cathode compartments. The electrolysis experiments were conducted in constant current mode using a DC power supply. All solutions were prepared using reverse osmosis purified water (Human Power III plus, South Korea) with a resistivity of 18 MΩ-cm.

For the electro-scrubbing process, a 50 cm<sup>2</sup> electrode area capacity divided plate and frame electrochemical cell was connected to a 40 cm high and 5.5 cm (i.d) column packed with 1 cm<sup>2</sup> of Teflon tubes as the packing material on top of the catholyte tank (1 L capacity), as in Fig.1 and the previous published literature [21]. The electrolyte solutions (500 ml) were circulated continuously to flow through the electrolytic cell at different flow rates (1 to 5 L min<sup>-1</sup>) using magnetic pumps. The catholyte solution as a scrubbing solution (electrolyzed mediator in a KOH solution) was pumped separately into the scrubber column at a flow rate of 3 L min<sup>-1</sup>. CF<sub>4</sub> gas (from RIGAS (1000 ppm), Korea) and N<sub>2</sub> mixtures, which were obtained by the



controlled mixing of air and  $\text{CF}_4$  gas using mass flow controllers (MFCs), were introduced to the bottom of the scrubber at a set gas flow rate. An online gas analyzer (FTIR) was attached to the scrubber exit to facilitate the instantaneous degradation measurements. Before each electrolysis experiment, the Ti electrode (cathode) was pretreated separately by an anodization process in 0.1 M  $\text{KNO}_3$  at a constant current of 1 A for 5 min. All experiments were conducted at room temperature ( $20 \pm 2$  °C).

### ***2.3 Quantification of mediator ion.***

The electrolyzed solution containing the  $\text{Cu}^{1+}$  or  $\text{Ni}^{1+}$  concentrations were determined using a potentiometric titration method [21]. In the present case, the electrolyzed sample solution was titrated against a standard  $\text{Fe}^{3+}(\text{CN})_6^{3-}$  (From Sigma Aldrich, USA) solution (0.001 M) and the potential variation was monitored using an ORP (oxidation/reduction potential) electrode (EMC 133, 6 mm Pt sensor electrode and Ag/AgCl reference electrode containing a gel electrolyte) connected to an iSTEK multimeter. The initial catholyte ( $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$ ) solution potential was approximately -170 mV, which was then decreased as electrolysis progressed at a constant current density. By titration against 0.001 M  $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$ , the initial ORP value showed that the  $\text{Fe}^{3+}$  concentration can be used to derive the concentration of  $\text{Cu}^{1+}$ .

### ***2.4 Analysis.***

Gas phase online analysis was performed using an online FTIR gas analyzer (from MIDAC Corporation, USA). Solution phase sample analysis was carried out by attenuated total reflectance – Fourier transform infrared (ATR-FTIR, Thermo scientific, Nicolet iS5, USA) spectroscopy using a 2  $\mu\text{L}$  drop of the reaction sample on the diamond sample holder to derive

the products. To understand the change in oxidation state of the metal ion and its influence in  $\text{CF}_4$  degradation process, ESR spectroscopy was performed with focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The ESR spectra were measured at the X-band ( $\sim 9.7$  GHz) and under liquid nitrogen conditions (77 K) with a Bruker EMX model spectrometer.

### 3. Results and discussion

#### 3.1 Generation of mediator.

Fig. 2A (curve a) shows the changes in ORP changes during the electrolysis of mediator precursor containing  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  the electrolyzed solution. The ORP value of the  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  electrolyzed solution was reached  $\sim -500$  mV from  $-50$  mV after 4h electrolysis could be  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  reduction. In order to crosscheck whether the  $\text{Ni}^{2+}$  reduction, though the  $\text{Ni}^{1+}$  ORP value found  $-800$  mV [21], occurred, the ORP value of only  $[\text{Ni}^{2+}(\text{CN})_4]^{2-}$  during electrolytic reduction was compared (Fig.2A curve b), where the ORP value reached immediately to  $-700$  mV indicating that  $\text{Cu}^{2+}$  is reduced instead of  $\text{Ni}^{2+}$  in the heterobimetallic complex ( $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$ ). To confirm whether  $\text{Cu}^{2+}$  is reduced, the electrolyzed solution of  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  was analyzed by ESR and the results are shown in Fig.2B. The ESR spectra showed a typical pattern for the polycrystalline  $\text{Cu}^{2+}$  ion having near axial symmetry with  $g_{xx} \approx g_{yy} (\sim 2.04)$  and  $g_{zz} (\sim 2.26)$  and  $A_{xx} \approx A_{yy} (\sim 35 \text{ G})$  and  $A_{zz} (\sim 190 \text{ G})$  values. The  $g$  values and  $A_{xx}$ ,  $A_{yy}$  and a large  $A_{zz}$  value, which is greater than  $140 \text{ G}$  confirmed the  $\text{Cu}^{2+}$  complex with a square-planar geometry [27] (Fig.2B curve a). On the other hand, its reduced monovalent  $\text{Cu}^{1+}$  species was ESR inactive. Therefore, at the same time, the electrolyzed  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  samples showed a reduced intensity without a change in the symmetrical

values indicating  $\text{Cu}^{1+}$  formation with square planar geometry (Fig.2B curve b). Interestingly, the  $\text{Cu}^{1+}$  concentration was increased with increasing electrolysis time (Fig.3), which was derived by potentiometric titration. The  $\text{Cu}^{1+}$  concentration can be generated electrochemically a maximum of 3.1 mM in 5 h electrolysis time in the bimetallic complex ( $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$ ) under the given conditions.

### 3.2 $\text{CF}_4$ degradation by MER.

Once the  $\text{Cu}^{1+}$  concentration reached approximately 3 mM by electrolysis, the electrolyzed solution of  $\text{Cu}^{1+}/\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  was pumped into the scrubbing column through the top of the scrubbing column. Subsequently, 10 ppm of  $\text{CF}_4$  was injected at  $0.2 \text{ L min}^{-1}$  into the bottom of the scrubbing column, while electrolysis was continued to regenerate the  $\text{Cu}^{1+}$ . Fig. 4 shows the results obtained under these conditions, where shows a decrease in  $\text{Cu}^{1+}$  concentration from 3.1 mM to 2.1 mM while inject 10 ppm of  $\text{CF}_4$  into the scrubber that then decreases further to 1.2 mM in 1h  $\text{CF}_4$  removal time. At the same time, there was almost 96% of feed  $\text{CF}_4$  removed initially and keep maintained around 93% removal during studied time 1 h (inset figure). This explains  $\text{CF}_4$  removal at room temperature by the electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  is possible. This 96%  $\text{CF}_4$  removal is not simply by absorption in to 10 M KOH solution because,  $\text{CF}_4$  absorption into a 10 M KOH solution reached saturation in 5 min [21]. The  $\text{Cu}^{1+}$  concentration variation during the  $\text{CF}_4$  removal process suggests that the  $\text{CF}_4$  removal reaction follows the MER by electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$ . The  $\text{Cu}^{1+}$  concentration started increased once the  $\text{CF}_4$  feed stopped confirms the  $\text{CF}_4$  removal sustainable by continuous generation of  $\text{Cu}^{1+}$  electrochemically.

Removal of  $\text{CF}_4$  was undertaken at different gas flow rates (Fig. 5). At the lowest gas flow rate of  $0.2 \text{ L min}^{-1}$ ,  $\text{CF}_4$  removal was almost 100%. However, this decreased to 26% with

increasing gas flow rates to 2 L min<sup>-1</sup>. This implies that the generation rate of Cu<sup>1+</sup> is insufficient to sustain CF<sub>4</sub> removal as CF<sub>4</sub> loading is increased. Mass transfer analysis confirmed that above the flow rate of 0.2 L min<sup>-1</sup>, a finite conversion rate of 13 to 18 μg CF<sub>4</sub> min<sup>-1</sup> was achieved independent of gas flow rate (Figure 6 curve a). When the rate of mass transfer in gas-liquid systems is independent of gas velocity, the process can be described as liquid-phase controlled, which is characteristic of separations comprising solutes with limited solubility, such as CF<sub>4</sub> [28]. In this study, the reduction of CF<sub>4</sub> could have been within the liquid film or within the bulk, in which case CF<sub>4</sub> absorption would have been facilitated without electrogenerated mediator (Fig.1 in ref. 21). Liquid-phase resistance to mass transfer may therefore be enhanced through optimizing the ratio between the scrubber recycle rate (or gas-to-liquid ratio) and electrochemical recycle rate, to increase the rate of reaction, and obviate resistance imposed by the low solubility of the non-reduced primary solute. Feed concentration was increased from 10 ppm to 30 ppm CF<sub>4</sub>, which reduced CF<sub>4</sub> removal efficiency from 95% to 30% (Fig.7). The time to steady-state increased to nearly 45 min at 30 ppm, which is ascribed to the sudden void of electrogenerated Cu<sup>1+</sup> through reaction with the increased CF<sub>4</sub> injection. Mass transfer analysis demonstrated a consistent rate of reaction at steady-state, which indicates that CF<sub>4</sub> degradation was zero order with respect to concentration (Figure 6 curve b), such that the rate of separation from the gas phase will be dependent upon the concentration of free reactant Cu<sup>1+</sup> in the liquid phase.

### **3.3 Product analysis.**

The comparative in-situ gas FTIR spectra (Fig.8 curve e) confirms the formation of CH<sub>3</sub>CH<sub>2</sub>OH during the degradation of CF<sub>4</sub> by MER process, where the standard CF<sub>4</sub> and

$\text{CH}_3\text{CH}_3\text{OH}$  were compared (Fig.8 curve a & b). At initial degradation process, there was observed no peak at  $\text{CH}_3\text{CH}_2\text{OH}$  frequency region (Fig.8 curve d) but  $\text{CH}_3\text{CH}_2\text{OH}$  peak found during its evolution timings (Fig.8 curve e) confirms the  $\text{CH}_3\text{CH}_2\text{OH}$  formation but, according to inset Fig.4, almost 96%  $\text{CF}_4$  removal was achieved from the beginning of the removal process. Also, no products were observed at the scrubber in the first 30 min (Fig.SI 1 curve a). After 30 min, a huge concentration of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) suddenly emerged at the scrubber exit at approximately 250 ppm (Fig.SI 1 curve a). In a similar time interval, trifluoroethane ( $\text{CH}_3\text{CF}_3$ ) began to exit around 10 ppm (Fig.SI 1 curve b). Note that ethanol and HF were produced from the beginning of the removal process while the electrogenerated  $\text{Co}^{1+}$  mediator was used to remove  $\text{CF}_4$  gas [21]. The  $\text{CF}_4$  removal process followed mediated degradation to soluble products that exited after a saturation point was attained, which could explain the late exit of  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CF}_3$ . Surprisingly, no HF gas was coming out of the scrubber or exit gas (inset figure of Fig.SI 1) could be due to  $\text{CH}_3\text{CF}_3$  intermediate formation by heterobimetallic complex ( $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$ ). Noteworthy that in case of only electrogenerated mediator  $[\text{Ni}^{1+}(\text{CN})_4]^{3-}$ , the  $\text{CF}_4$  removal followed  $\text{COF}_2$  intermediate pathway [21] to produce ethanol. Also, the  $\text{CH}_2\text{CH}_2\text{OH}$  formation found only at 0.2 L/min gas flow rate and at higher gas flow rates 1 and 2 L  $\text{min}^{-1}$ , there found no  $\text{CH}_3\text{CH}_2\text{OH}$  peak but  $\text{CH}_3\text{CF}_3$  peak appeared (Fig.SI 2 & 3) at its respective frequency region additionally support the  $\text{CH}_3\text{CH}_2\text{OH}$  formation only at low gas flow rate and also the reaction stopped at intermediate formation. The scrubbing solution underwent an ATR-FTIR analysis after the electro-scrubbing process was completed and reaction solution showed only  $\text{CH}_3\text{CH}_2\text{OH}$  present (-O-H and -C-O stretching frequencies well matched with the instrument library  $\text{CH}_3\text{CH}_2\text{OH}$  sample) in solution (Fig. SI 4), confirming that the reaction product is  $\text{CH}_3\text{CH}_2\text{OH}$ . Many electrochemical

reports have shown that CFCs form  $\text{CH}_4$  and fluorine-reduced derivatives, such as  $\text{CF}_3\text{CH}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_3\text{F}$ , and  $\text{CF}_2\text{CFCl}$  [17-20] but, there are no reports on the formation of  $\text{CH}_3\text{CH}_2\text{OH}$  during the degradation of  $\text{CF}_4$ . Recently, direct ethanol formation was observed on a copper electrode during the reduction of  $\text{CO}_2$  through carbon dioxide dimer formation [29,30]. Similarly, a carbon tetrafluoride dimer could have formed via the electrogenerated  $\text{Cu}^{1+}$ , which might have easily hydroxylated to ethanol, because the scrubbing solution is 10 M KOH, as shown by the proposed scheme 1. The possibility of dimerization was confirmed by the additional product  $\text{CF}_3\text{CH}_3$  (Fig.8 curve b) found at the scrubber exit, which may be due to incomplete reaction or intermediate formation.

#### 4. Conclusions

Electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  successfully degraded  $\text{CF}_4$  to ethanol without forming HF at room temperature. The electrogeneration of  $\text{Cu}^{1+}$  from the hetero-bimetallic complex of  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  was identified by ORP variation and confirmed the same by ESR spectroscopy analysis. The  $\text{Cu}^{1+}$  concentration variation during the injection of  $\text{CF}_4$  into the scrubber column or the  $\text{CF}_4$  removal process confirmed the degradation of  $\text{CF}_4$  follows MER process. The online gas phase and offline solution phase FTIR analyses results confirmed that  $\text{CH}_3\text{CH}_2\text{OH}$  is a final product along with an intermediate or incomplete product  $\text{CF}_3\text{CH}_3$  without corrosive product HF during the degradation of  $\text{CF}_4$  using the electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  in a highly KOH medium. Independent of mass transfer coefficient with feed  $\text{CF}_4$  concentration confines the degradation follows zero order kinetics and chemical reaction controlled process, which enables to help scale-up the process.

**ACKNOWLEDGEMENT**

This investigation 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. NRF-2017R1A2A1A05001484).

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**Figure captions**

Fig.1 Schematic experimental setup used to degrade  $\text{CF}_4$  at wet-scrubber by electrochemically generated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$

Fig.2 (A) Oxidation/reduction potential (ORP) variation during electrolysis of (a) 50 mM  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  and (b) 50 mM  $[\text{Ni}^{2+}(\text{CN})_4]^{2-}$  in 10 M KOH solution. Electrolysis conditions: Electrodes ( $4 \text{ cm}^2$ ) = Pt (anode) and anodized Ti (cathode); Current density  $-30 \text{ mA cm}^{-2}$ ; Solution flow rate =  $70 \text{ ml min}^{-1}$ .

(B) ESR spectra of frozen  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  in a 10 M KOH solution (a) before and (b) after electrolysis. The electrolysis conditions were the same as in legend of Fig.2A.

Fig.3 Formation efficiency of  $\text{Cu}^{1+}$  from  $\text{Cu}^{2+}[\text{Ni}^{2+}(\text{CN})_4]$  during electrolysis in 10 M KOH solution. The electrolysis conditions are the same as in the legend of Fig.2A..

Fig.4  $\text{Cu}^{1+}$  concentration variation during MER of  $\text{CF}_4$  gas at electro-scrubbing by scrubbing a solution of electrolyzed  $\text{Cu}^{2+}/\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-/0}$  solution. Inst figure shows  $\text{CF}_4$  degradation efficiency variation with time. Conditions: Feed concentration of  $\text{CF}_4$  = 10 ppm; Gas flow rate =  $0.2 \text{ L min}^{-1}$ ; Scrubbing solution flow rate =  $3 \text{ L min}^{-1}$ . Solution flow rate to electrolytic cell =  $2 \text{ L min}^{-1}$ ; Current density =  $30 \text{ mAcm}^{-2}$ ; Electrodes area =  $50 \text{ cm}^2$ .

Fig.5 Effect of the gas flow rate (mentioned in the figure) with time on the removal of  $\text{CF}_4$  using electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  in a 10 M KOH solution at electro-scrubbing. The remaining experimental conditions are the same as in the legend of Fig.4.

Fig.6 Mass conversion rate with  $\text{CF}_4$  feed concentration (a) and gas flow rate (b) during its degradation at electro-scrubbing by electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  in 10 M KOH solution. The electrolysis and electroscrubbing experimental conditions are the same as

in the legend of Fig.4.

Fig.7 Effect of the  $\text{CF}_4$  feed concentration variation with time on its removal by electrogenerated  $\text{Cu}^{1+}[\text{Ni}^{2+}(\text{CN})_4]^{1-}$  in 10 M KOH solution by electro-scrubbing. The remaining experimental conditions are the same as in the legend of Fig.4.

Fig.8 Real time FTIR spectra during the removal of  $\text{CF}_4$  at different conditions for product  $\text{CH}_3\text{CH}_2\text{OH}$  identification: (a) Reference FTIR for  $\text{CF}_4$ ; (b) Reference FTIR for  $\text{CH}_3\text{CH}_2\text{OH}$ ; (c) During direct feed on  $\text{CF}_4$ ; (d) During the MER of  $\text{CF}_4$  at 30 min; (e) During the MER of  $\text{CF}_4$  at 60 min. The remaining experimental conditions are the same as in the legend of Fig.4.

Figures

Fig.1

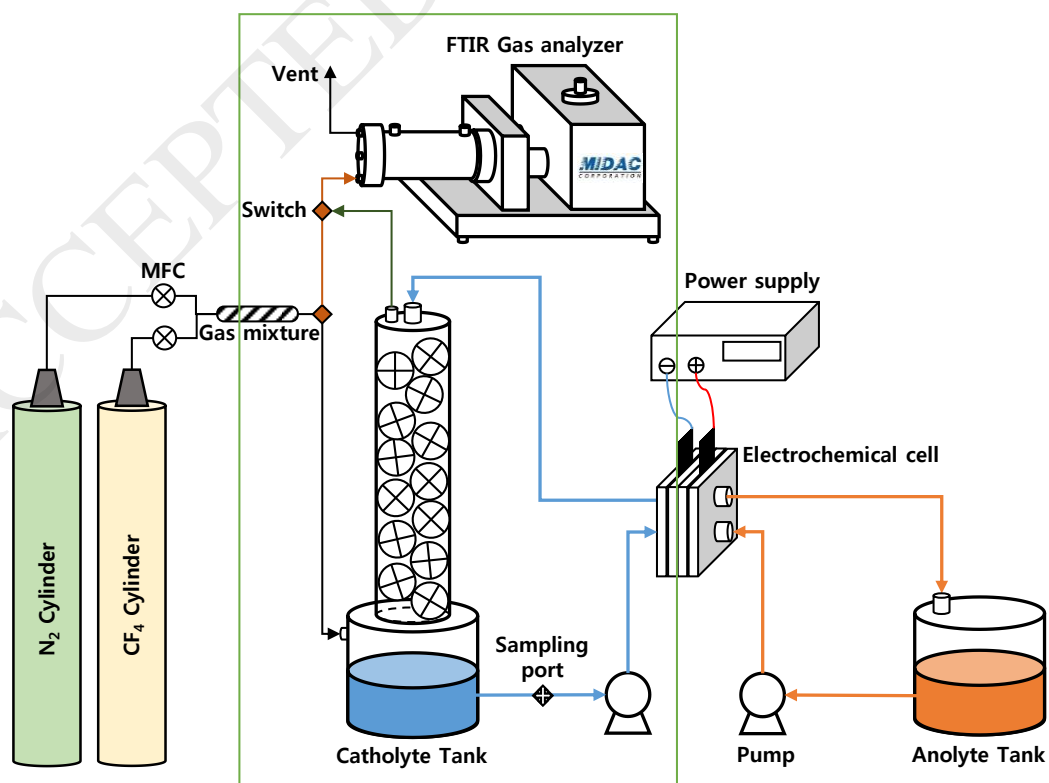


Fig.2

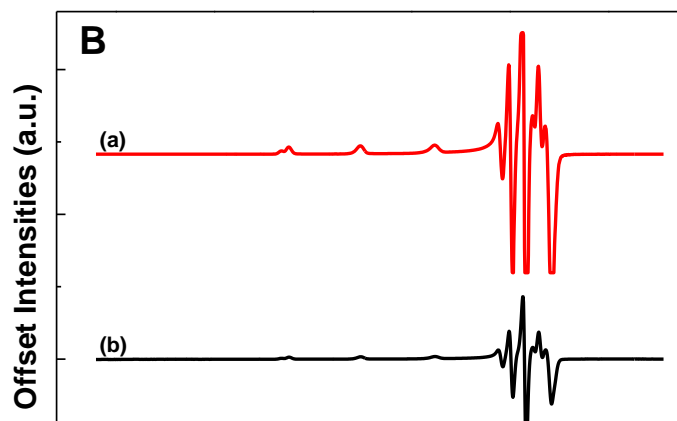
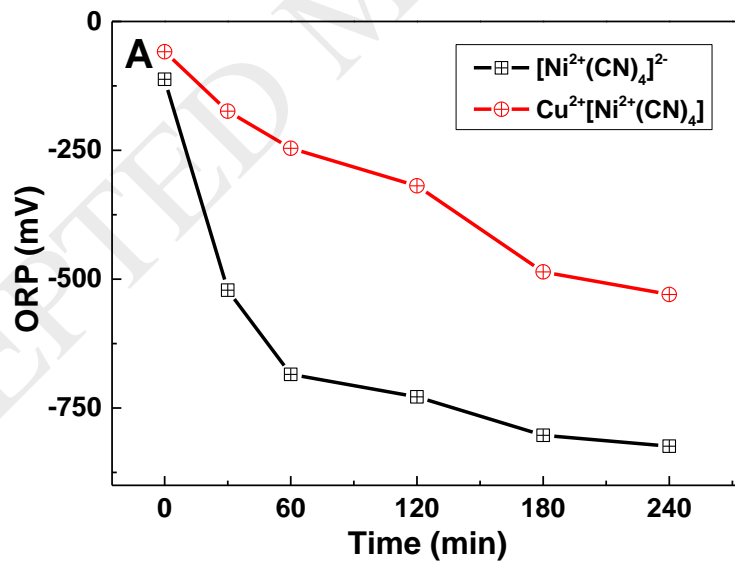


Fig.3

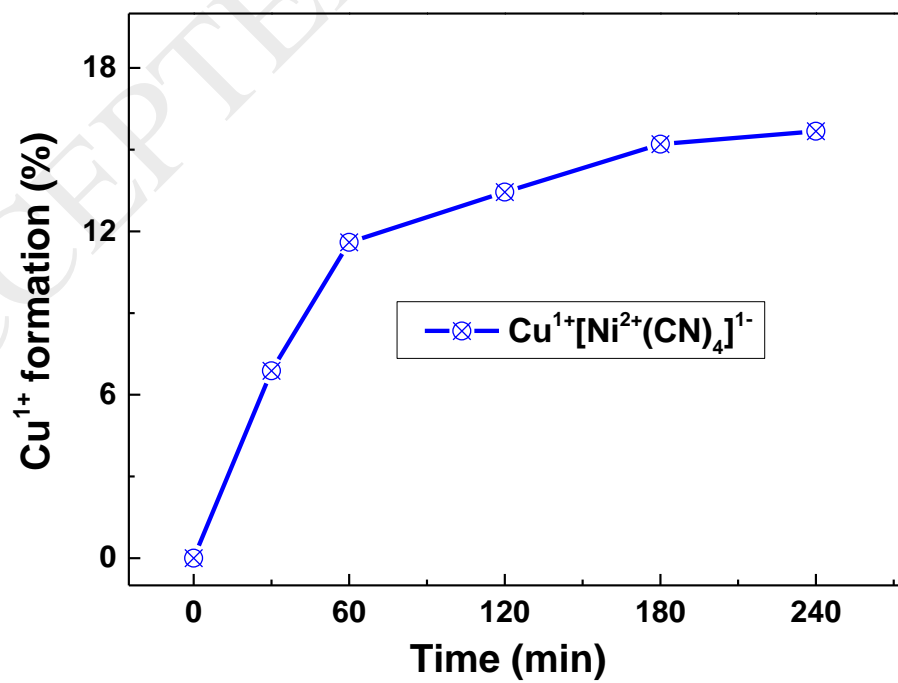


Fig.4

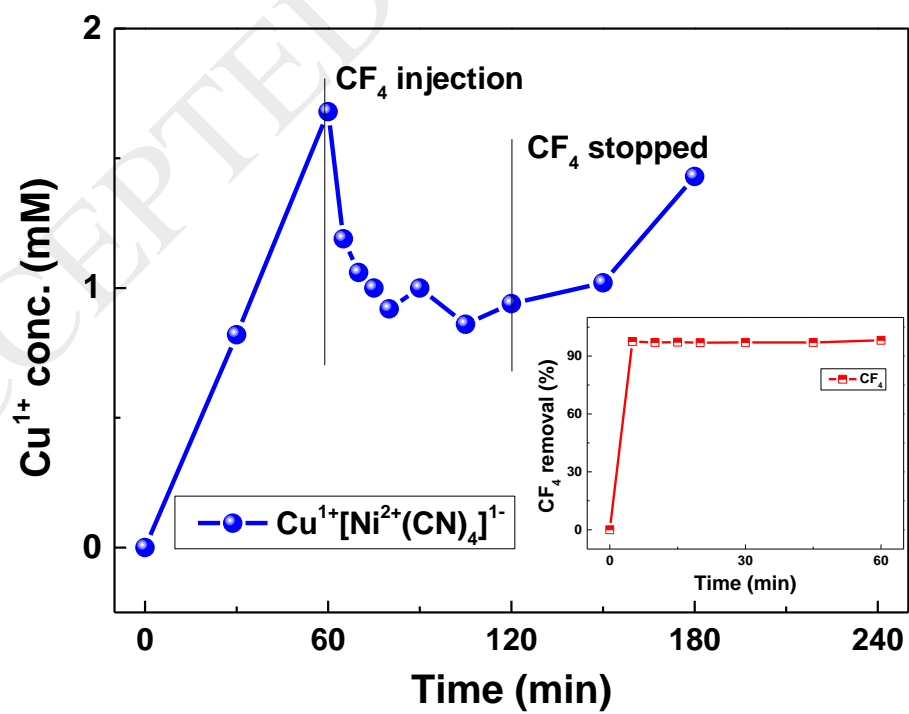


Fig.5

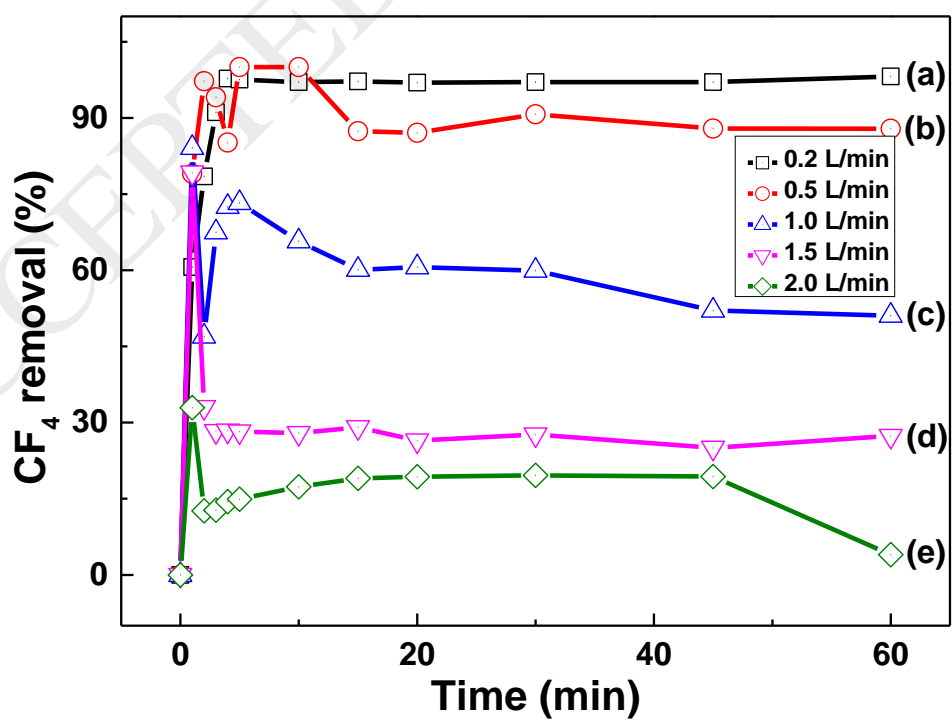


Fig.6

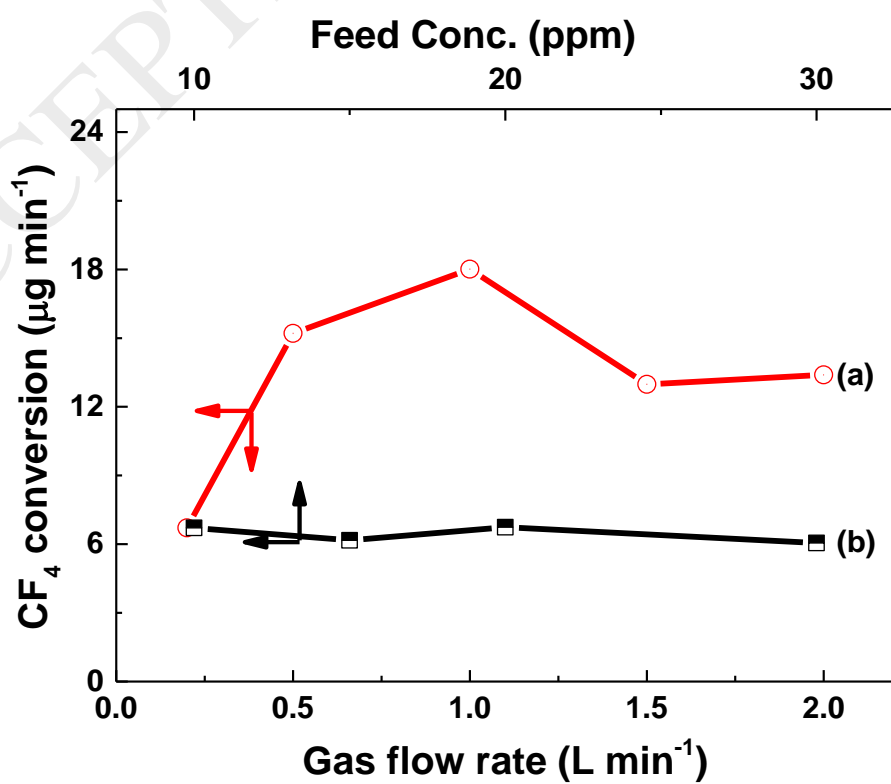




Fig.7

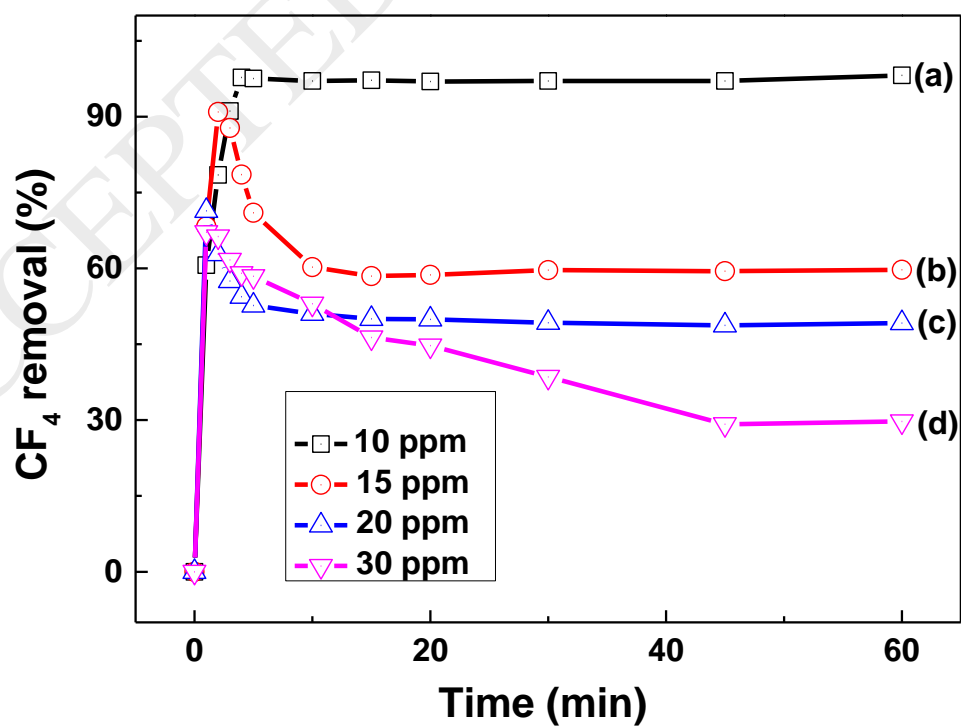
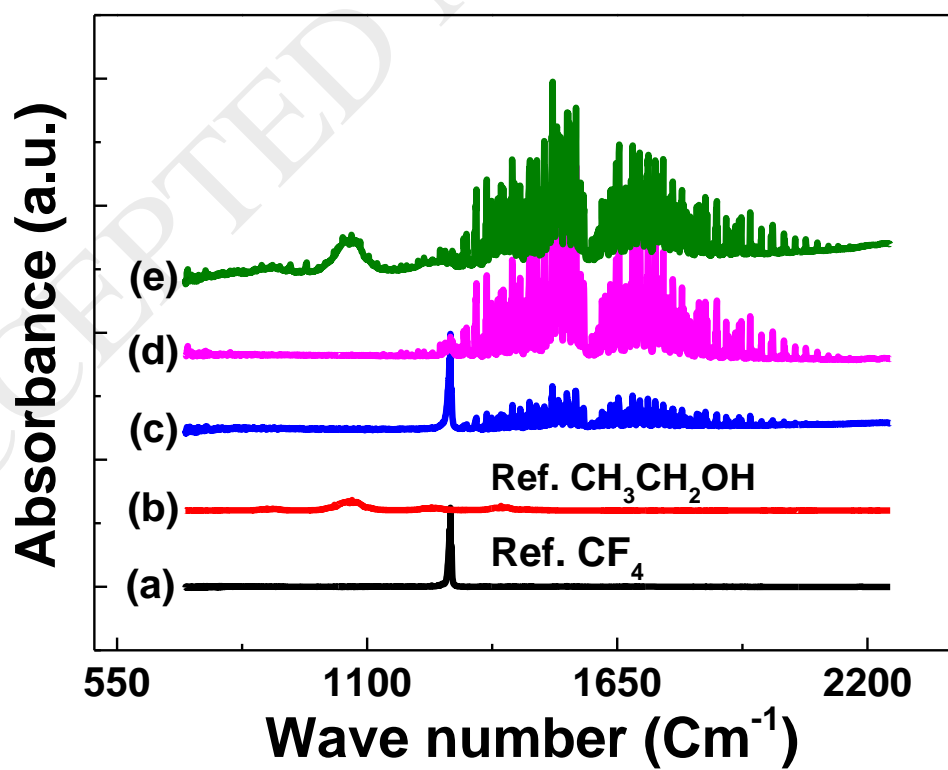
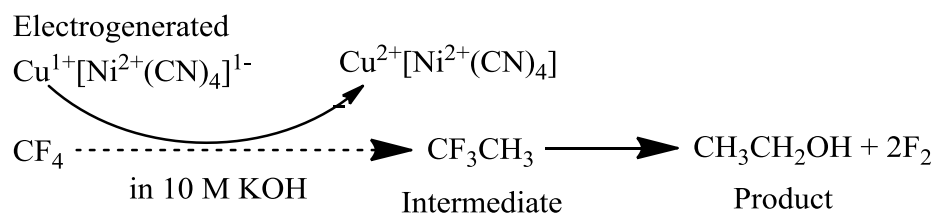


Fig.8





Scheme 1 Plausible reaction pathway for  $\text{CF}_4$  degradation to ethanol

# Sustainable degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced electron mediator within electro-scrubbing

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2018-02-21

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Muthuraman G, Ramu AG, Cho YH, McAdam EJ, Moon IS, Sustainable degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced electron mediator within electro-scrubbing, *Journal of Industrial and Engineering Chemistry*, Volume 63, 25 July 2018, Pages 275-280

<https://doi.org/10.1016/j.jiec.2018.02.025>

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