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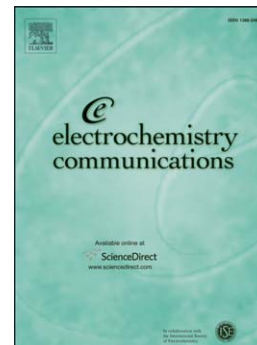
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Gas-phase volatile organic chloride electroreduction: a versatile experimental setup for electrolytic dechlorination and voltammetric analysis

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Abstract

Silver is a well-known and largely studied electrocatalytic material for (hydro)dehalogenation reactions of organic halides, a class which includes several priority pollutants. Silver nanoparticles are particularly attractive since exhibit similar or even better performances than bulk silver allowing a significant reduction of precious metal loading. In this study the hydrodehalogenation of CHCl_3 is selected as model reaction in order to evaluate the electrocatalytic activity of 2-15 nm silver nanoparticles. For the electrochemical characterization a versatile experimental setup was purportedly in-house designed and assembled that allows both cyclic voltammetry and electrolysis investigations. All the tests are performed in aqueous solution using a gas diffusion electrode as working cathode. The progressive conversion of gaseous trichloromethane to less chlorinated compounds is quantitatively evaluated in terms of concentration Cl^- ions produced in the aqueous electrolyte solution.

Keywords: Ag nanoparticle, dehalogenation, gas diffusion electrode, silver cathode, trichloromethane,

1. Introduction

Volatile organic halides (VOH) are a large family of substances that show very high toxicity and are present in a wide variety of wastes: from concentrated organic solutions and emulsions to very dilute aqueous phases, to airborne streams. The development of suitable treatment methodologies constitutes a serious challenge. Among the various methods, electroreductive hydrodehalogenations are very attractive because of their mild conditions, the possible production of value added substances, the rather good conversion yields and low energy consumptions thanks to the use of specific metallic (e.g. Ag, Pd, Cu, Pt) [1,2,3,4,5,6] and alloy [7, 8,9] cathodes. Among them, silver has been found to possess extraordinary electrocatalytic properties toward the C-X (X = Cl, Br, I) bond cleavage for synthetic [10,11,12,13,14] and environmental [15,16,17,18,19] applications. Therefore, in the last 10-15 years the electrocatalytic properties of silver, as cathode material for the VOH electroreduction, have been largely studied [2,15, 19,20,21,22]. In particular the attention is focused on nanosized particles since they exhibit enhanced activity in comparison with bulk silver allowing the use of composite materials with very low metal loading [21,2]. The present contribution reports the preparation, characterization and use of Ag nanoparticles (AgNP) obtained by chemical reduction of AgNO_3 by trisodium citrate dehydrate [23]. The already assessed electrocatalytic activity of AgNP's for the electroreduction of trichloromethane model substrate in aqueous media [2] is now applied in a new electrochemical cell setup adopting a Gas Diffusion Electrode (GDE) as sensor/working cathode for the direct gas-phase electroreduction of CHCl_3 . The electrochemical performance of AgNP-based Gas Diffusion Electrodes (AgNP-GDE), is evaluated by both cyclic voltammetry (CV) and electrolysis tests. The results are discussed in terms of CV response and CHCl_3 to CH_4 conversion.

2. Experimental

All the electrochemical tests are carried out with Amel 5000 driven by Corrware software Scribner Associate Inc. and all the chemicals were purchased from Sigma– Aldrich and used without further purification. For all aqueous preparations MilliQ water (Millipore system) was used.

2.1 Ag nanoparticles

AgNPs were prepared following the procedure reported in [23], briefly: 2 μL of 12.5 mM aqueous ascorbic acid is added to boiling water. After one minute, a precursor solution (1.25 mL AgNO_3 1wt%, 5 mL trisodium citrate dihydrate 1 wt%, 2.2 μL KI 7 mM, 6.25 mL H_2O) was added and maintained for 1 h at boiling temperature under vigorous stirring.

AgNPs were supported on carbon powder (Vulcan Cabot XC72-R) oxidatively pretreated as indicated in [24]. This procedure ensures not only a better affinity between Ag and the carbon matrix, allowing an effective Ag clamping and homogeneous dispersion, but increase the presence of oxo-groups which impart hydrophilicity to the carbon surface. A known amount of powder is added to the silver colloidal system to yield the selected silver-to-carbon ratio (Ag 5 wt%).

2.2 GDE preparation and electrochemical cell

The GDE are prepared on a graphite fiber cloth acting as both GDE support and electrical collector. Two different carbon mixtures were used, Shawinigan Acetylene Black (SAB)/PTFE 50:50 by mass and Vulcan XC72-R/ PTFE 50:50 by mass. The mixtures are pasted over the graphite disk cloth ($\varnothing = 24$ mm) one layer at a time, alternating sides as described in [21]. AgNP-GDE were prepared in the same way using the Ag-NP modified VulcanXC72R matrix.

Please insert Fig. 1 here

The experimental setup used in this work places the GDE (4.5 cm^2 of geometrical area) in direct contact with the solution. Fig. 1 schematizes the working electrode (WE) structure and the entire experimental setup. The WE consists in a glass tube closed at the bottom by the GDE (disk D) and at the top by a air-tight cover with gas entrance (A) and exit (B). The gas feed (N_2 or CHCl_3 -saturated N_2) is delivered right at the surface of the GDE. The current collector is a carbon cloth ring (C) held in position with the same Sovirel^R that fixes the GDE. The sketched electrolysis setup includes: (1) the presaturation system (two Drechsel bottles+demister) to saturate the N_2 gas with CHCl_3 at room temperature; (2) the electrochemical cell, in the classic 3-electrode configuration (WE, Pt counter electrode and double-bridge Saturated Calomel Electrode as reference) in order to control the experiment either potentiostatically or galvanostatically. The exhausted gas mixture, exit (B), passes through the NaOH solution trap (3) to collect the possible gaseous HCl reaction product. The flow-rate of the CHCl_3/N_2 mixture was adjusted at 6 - 8 mL/min, which corresponds to about 0.9 - 1.2 $\mu\text{mol/s}$ of CHCl_3 . The constancy of the flow-rate was periodically checked during each electrolysis run. The electrolyses were driven intensiostatically, at three different current densities (2.2, 4.4, 6.6 mAcm^{-2}). Before each run the background electrolyte and the WE were de-aerated by N_2 . Afterwards, the WE was shortly conditioned with the $\text{N}_2 + \text{CHCl}_3$ reaction mixture. At the end of each run, the presence and concentration of chlorides in the electrolyte solution and in the NaOH trap were detected and determined by potentiometric AgNO_3 titration.

3. Results and discussion

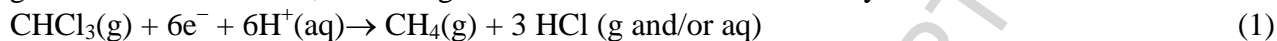
3.1 GDE Cyclic Voltammetry

The versatile experimental setup described above allows an easy GDEs characterization by CV. As reported in Fig. 2 CVs were performed both in the presence and in the absence of CHCl_3 . In the background electrolyte (KClO_4 0.1 M) the AgNP-GDE shows the typical charge/discharge of the double layer capacitance, while in the presence of CHCl_3 the net current increase clearly indicates the ongoing electroreduction of the substrate. The observed reaction was then confirmed by galvanostatic electrolyses on gaseous CHCl_3 .

Please insert Fig. 2 here

3.2 Electrolysis

The electrolyses are aimed at demonstrating that CHCl_3 can be reduced at the GDE when fed as gaseous stream mixture, according to overall reaction stoichiometry:



and that the resulting HCl is almost exclusively collected in the aqueous phase, according to the energy of its dissolution reaction. In principle, the HCl could be theoretically found: in the exiting gas stream, where would be collected by the NaOH trap, and in the electrolytic solution.

Obviously, methane and other possible partially chlorinated products would remain in the gas stream.

Please insert Table 1 here

The results are summarized in Table 1, which collects for each run current density, electrolysis time, total quantity of charge, the final chloride content determined in the background electrolyte and the corresponding $\text{Cl}^-/\text{CHCl}_3$ mol ratio. Samples of the NaOH trap and of the electrolyte solution are taken right before and right after each run, for determining the chloride content by silver nitrate titration. The Cl^- content of the NaOH trap samples was below the detection limit of the method, provided that the titrations be carried out immediately after sampling in order to avoid the favorably slow $\text{S}_{\text{N}}2$ reaction between OH^- and CHCl_3 to produce Cl^- , which would alter the results.

The first two runs were planned to be performed at three different current densities for 900 s each. However, in both cases, the last segment at 6.6 mAcm^{-2} had to be stopped because the cell voltage rapidly increased to reach the compliance limit of 10 V. Hence, the 3rd run was performed in a single stage at 4.4 mAcm^{-2} , thus allowing the completion of the 1-hour process at a stable cell voltage. Note that parallelly the $\text{Cl}^-/\text{CHCl}_3$ mol ratio raises from about 2 to 2.5. Taking into account the preliminary nature of these experiments, this ratio represents a lower limit, that can very likely lead to the 100% CHCl_3 to CH_4 conversion. This outcome is even more interesting when considering the low silver loading and will prompt our future more detailed investigations toward larger scale applications.

4. Conclusions

Silver nanoparticles were successfully applied to the electroreductive dehalogenation of organic halides in GDE systems, pointing to very high conversion yields. Work is still in progress to extend these encouraging results both in terms of increasing electrode size and/or current densities.

Nonetheless, the preliminary testes clearly show the good electrocatalytic activity of carbon-supported silver nanoparticles. The key materials were developed together with the investigation tools that leads to a versatile experimental setup combining the possibility of carrying classical cyclic voltammetry analysis and electrolysis experiments.

Acknowledgments.

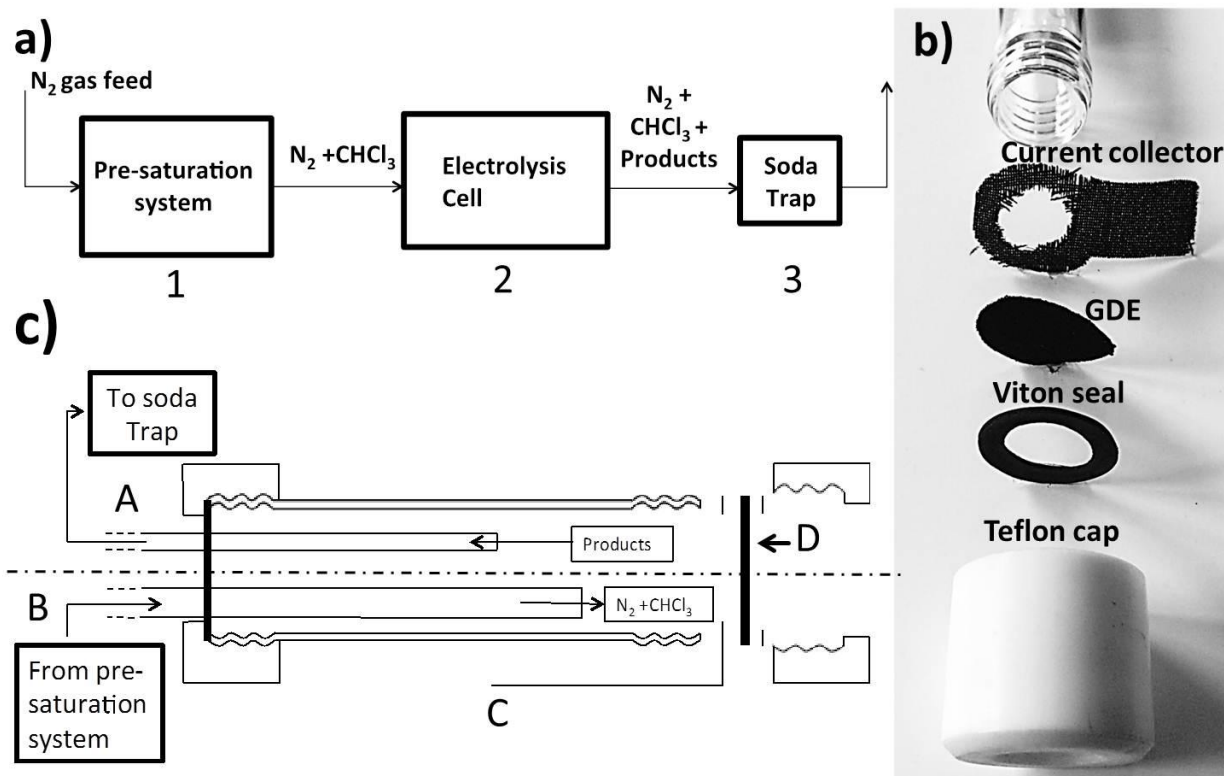
Financial support from the Università degli Studi di Milano is gratefully acknowledged. O.L. and C.L. are grateful to the University of Milan for their post-doc fellowship. We acknowledge the contribution to the experiments of Mr. Henri Encontre, on leave from École Polytechnique Fédérale de Lausanne

Figure captions:

Fig. 1: Scheme of the GDE working electrode and process flow chart.

Fig. 2: CVs at AgNP-GDE 5%Ag WE, $v_{\text{scan}}=20$ mV/s, in aqueous KClO₄ 0.1 M; continuous line: background electrolyte; dashed line: in the presence of 10mM CHCl₃.
Table 1: electrolysis results.

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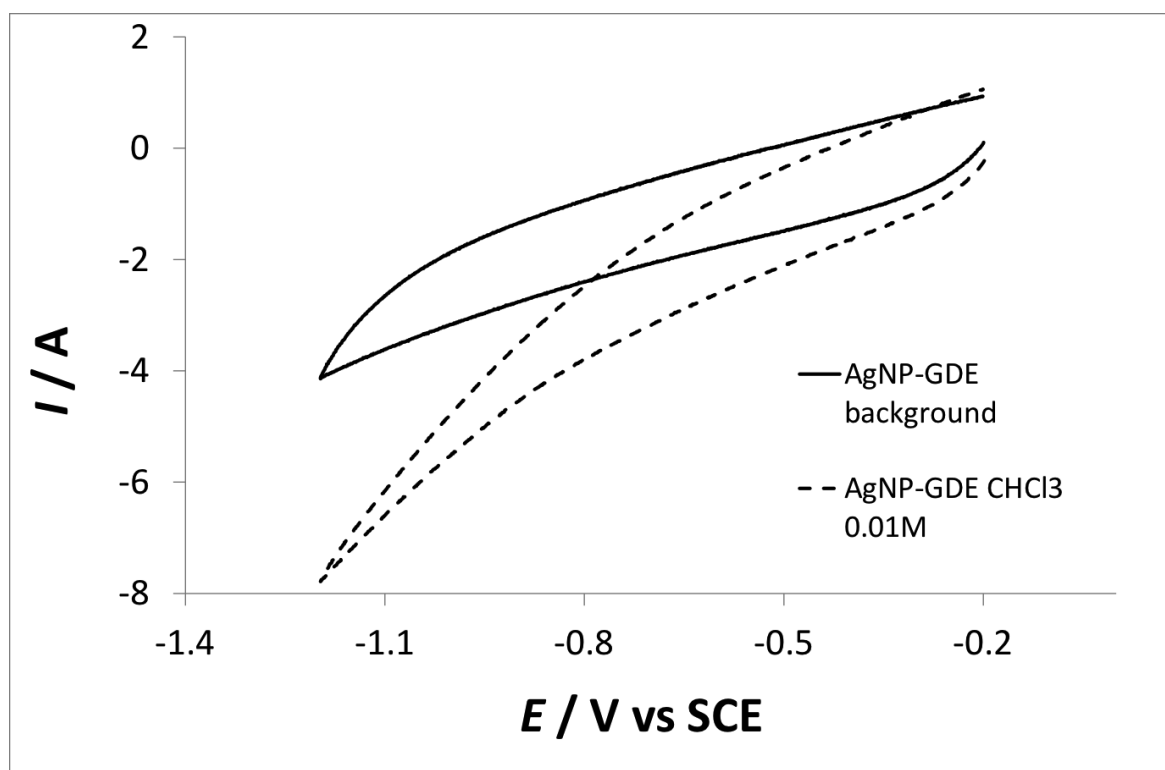


Figure 2

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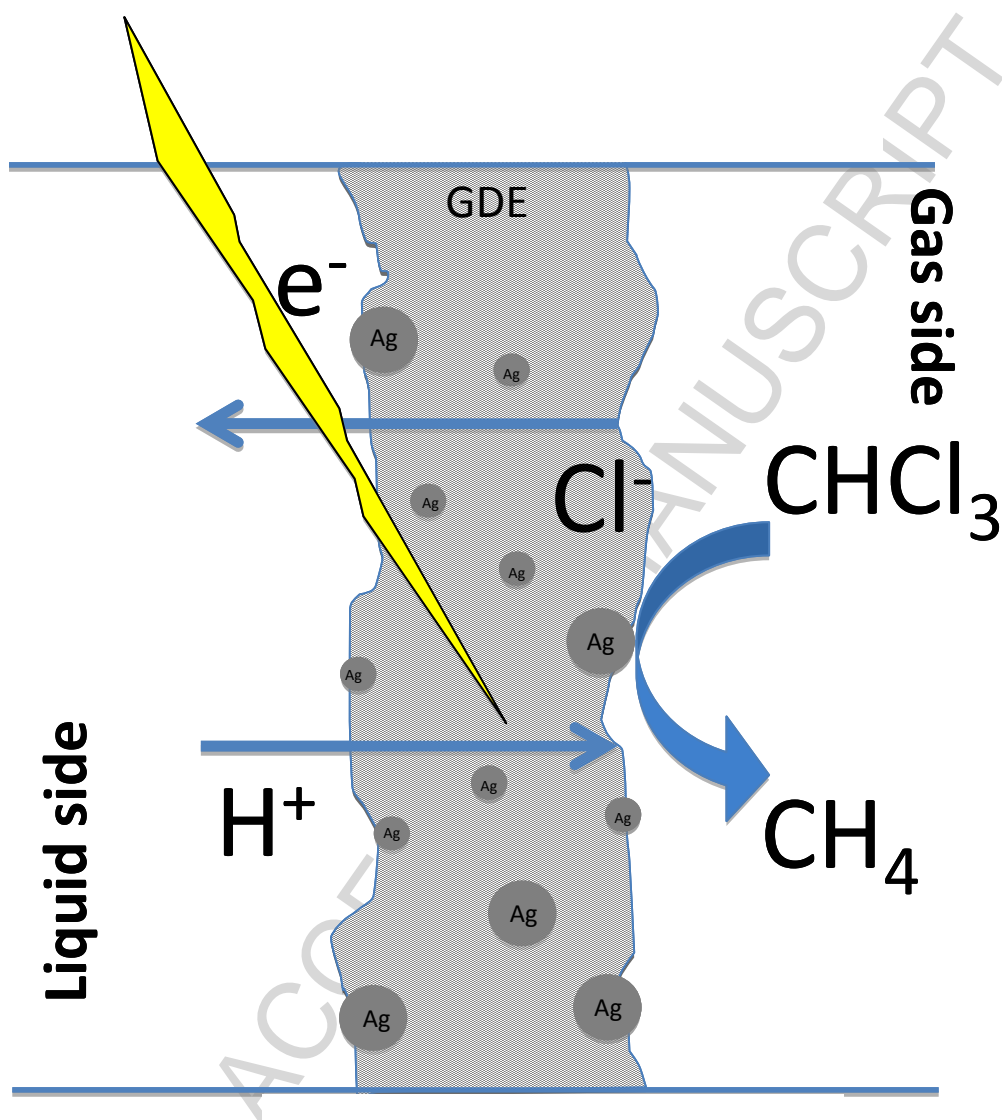
Run	j (mAcm ⁻²)	t (s)	ΣQ (C)	n_{Cl^-} (mmol)	$n_{\text{Cl}^-}/n_{\text{CHCl}_3}$
	2.21	900			
1	4.42	900	45	0.163	2.11
	6.63	594			
	2.21	900			
2	4.42	900	39	0.137	2.03
	6.63	424			
3	4.42	3600	72	0.310	2.49

Table 1

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Graphical abstract



Rondinini – Highlights

- a versatile setup for voltammetry and electrolysis on gas-phase organic chlorides
- synthesis and use of Ag nanoparticles (AgNP) for Gas Diffusion Electrodes (GDEs)
- AgNP-GDEs as working cathodes for electroreductions
- AgNP-GDEs are used to detect/dehalogenate trichloromethane model substrate

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