"Egg of Columbus": Single-Step Complete Removal of Chloride Impurities from Ionic Liquids by AgCl Deposition on Silver Electrode

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Abstract. Chloride impurities in ionic liquids (ILs), which can be present even in huge amounts depending on the IL synthetic route, are particularly critical for electrochemical processes; thus, their abatement is often mandatory. However, while their analytical quantification has been the subject of many studies involving a variety of techniques, the so far available processes for their abatement are still unsatisfactory, having low efficiency, and/or involving multiple steps, and/or being far from mild and easily scalable.

In this context, like an "egg of Columbus", a quite simple and safe process for chloride abatement in ILs is proposed, practically coinciding with the electrolytic preparation of a Ag|AgCl electrode. It proceeds in a single step, at room temperature, at very low potentials, with nearly ideal current efficiencies, and with negligible side effects on the electrolyzed IL. The chloride impurities are quantitatively captured and accumulated on the silver wire and eliminated by simply removing the resulting Ag|AgCl electrode from the solution, with no need of subsequent treatments.

Keywords Ionic liquids, chloride removal, electrodeposition, silver electrode, silver chloride

1. Introduction

Ionic liquids (ILs) are increasingly popular media providing an advantageous alternative to VOCs in many chemical and electrochemical processes [1-3]. For most applications their purity is a fundamental issue. Besides the concern for residual water content, common preparation methods can result in significant amounts of *e.g.* acidity and/or halide anions. Unfortunately, intrinsic IL features such as low vapour pressure and low melting point make it critical to remove impurities by distillation or recrystallization; also washing or extraction procedures cannot afford halide-free ionic liquids [4,5].

Halide impurities in ILs are particularly critical for electrochemical processes, for instance considering the nucleophilicity of chloride anions, their influence on pseudoreference electrode potentials, their possible involvement in doping/undoping processes in polymerizations, etc.

Such a huge impact of the IL halide impurities has prompted application of different analytical techniques to their quantitative determination, including voltammetry on Pt [6], glassy carbon (GC) [4], Au [4], and Ag [4]. In particular, Ag is the only surface affording an oxidative preconcentration step

$$\mathrm{Ag_{(s)} + Cl^-_{(IL)} \rightarrow AgCl_{(s)} + e^-} \qquad (1)$$

to be followed by cathodic stripping; this results in a lower chloride limit of detection (for instance, among values reported in the literature, 0.16 ppm [4] in $BMIMBF_4$, to be compared with 2.7 ppm and 100 ppm by square wave voltammetry on GC [4] and Pt [6], respectively).

On the other hand, very few approaches to the electrochemical abatement of IL halide impurities have so far appeared. One of them involves Cl^- electroxidation to Cl_2, on Pt anode, at constant potential, in a divided cell [6]. A more recent, similar study deals with both Cl^- and Br^- concurrently [5], in a cell divided by an anion exchange membrane, the cathodic compartment being filled with HNO_3 or HBF_4 solutions in order to provide convenient anions to replace the eliminated halide ions. The working potential is +1.6 V (*vs.* Ag|AgCl) at room temperature in the bromide case and +1.4 V (*vs.* Ag|AgCl) at 80 °C in the chloride one. The electrolytic process must be followed by a treatment with ethylene gas to capture the electrogenerated Br_2 and Cl_2; the resulting halogenated products are then volatilized under vacuum. On the whole, the working conditions (high potential and temperature, strong acid, ethylene gas, halogenated products to be volatilized, multiple steps) appear far from mild and easily scalable.

The turning point could be the possibility of easy, safe disposal of the oxidation products.

In the present paper, a very simple, but winning solution is presented, which consists in performing the electroxidation process on a silver anode.[1] The oxidation reaction (eq 1) allows to operate at a very low potential and room temperature, while the AgCl oxidation product directly grows on the Ag electrode as a compact, stable layer. Actually the process coincides with the electrolytic production of a Ag|AgCl electrode and an easy complete chloride removal is achieved by simply removing it from the solution.

Concerning the counter reaction, the choice of a Pt cathode in the presence of a sufficient amount of residual water in the IL implies hydrogen evolution [5] with concurrent pH increase; this could be beneficial to the IL, too, since most ILs have H^+ impurities besides halide ions.

The Cl^- removal can be monitored by a second smaller Ag electrode, provided that suitable calibration is previously made under the same conditions.

2. Materials and Methods

Voltammetric measurements (cyclic voltammetry, CV, differential pulse voltammetry, DPV, cathodic stripping voltammetry, CSV) and constant potential electrolyses were performed using an Autolab PGSTAT128 or PGSTAT302N potentiostat/galvanostat (EcoChemie, The Netherlands), managed by a PC with GPES software. All experiments were carried out in a three-electrode mini-cell with 3 or 4 cm^3 of commercially available ionic liquids. Two samples of different purity of 1-butyl-3-methylimidazolium hexafluorophosphate, $BMIMPF_6$ (≥97.0%, Aldrich; and ≥98.5%, Fluka) and one of the corresponding tetrafluoroborate salt, $BMIMBF_4$ (≥98% "BASF-Quality", Aldrich) were considered.

Voltammetric measurements employed a Teflon-embedded Ag disk (Amel, surface area 0.071 cm^2) or glass-embedded GC disk (Metrohm, surface area 0.031 cm^2) as working electrode, a Pt wire as counter electrode and an aqueous saturated calomel (SCE) as reference electrode inserted into a glass jacket, filled with IL, ending in a porous frit to prevent water and chloride leakage in the working solution. Calibration plots for the quantification of IL chloride impurities were obtained starting from the purest $BMIMPF_6$ available to us (98.5% Fluka), over a wide range of added chloride concentrations ($5\times10^{-6} \div 3\times10^{-2}$ mol dm^{-3}) obtained from a standard solution of tetraethylammonium chloride, TEACl (98.0%, Fluka) dissolved in the same IL. Techniques of decreasing sensitivity with increasing chloride concentration were applied, *i.e.* CSV, DPV, and CV, on Ag electrode (Figure 1), exploiting the oxidation process (eq 1), either as accumulation step in CSV, or as direct diffusive peak, at $E_{p,Ag} = -0.15$ V (*vs.* SCE) in DPV (yielding simple peaks in the lower concentration range and more complex ones at the higher concentrations) and in CV. The pulsed technique parameters were: conditioning potential −0.4 V (*vs.* SCE) for 30 seconds, equilibration time 5 s, modulation time 0.05 s, modulation amplitude 0.05 V, interval time 0.1 s, step potential 0.001 V; for the stripping analysis after the conditioning period a preconcentration step was performed at +0.4 or +0.1 V (*vs.* SCE) for a specified time period. Cyclic voltammetry was recorded at a scan rate of 0.2 V s^{-1}.

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[1] Surprisingly, the peculiar affinity of silver for chlorides has so far been exploited for abatement purposes only in a metathesis reaction aimed to lower the IL chloride and bromide content [5]; the reaction, however, produces an equimolar amount of silver halide that has to be separated from the IL medium, a quite difficult step.

In the highest concentration range, GC was also employed, since it implies the reaction

$$2Cl^{-}_{(IL)} \rightarrow Cl_{2(IL)} + 2e^{-} \qquad (2)$$

at $E_{p,GC} = +1.25$ V (*vs.* SCE), which does not involve oxidation of the electrode surface, which could turn out to be kinetically limiting in the case of high chloride amounts and high scan rates. Good linearity was observed for all concentration ranges with the corresponding techniques, using either current or charge as analytical signal (Figure 1). Since peak currents are quite lower than in water or organic solvents on account of the high IL viscosity, the detection limits are of course much higher than in water. In the CSV case it is of the order of 5×10^{-6} M with our chosen protocol, but could be lowered by increasing the accumulation time.

For bulk electrolysis aimed at Cl^{-} abatement, a Ag pigtail wire (1 mm diameter, 13-15 cm length) was employed as anode and, when necessary as discussed below, the Pt wire was inserted into a second jacket in order to obtain a separated cathodic compartment. Both electrolyses and CSV preconcentration steps were carried out under constant stirring, while there is no need of deareation.

3. Results and Discussion

To evaluate the chloride amount before, during, and after the abatement process, the multitechnique voltammetric protocol on Ag and GC electrodes described in the Materials and Methods section was applied, similar to one previously proposed in the literature [4], but with some modifications, particularly the much lower accumulation potential. The linear dynamic ranges (either considering current or charge) afford safe application of the standard addition technique (SAT) for quantification of chloride concentration, of course selecting the appropriate voltammetric technique according to the concentration range. A chloride content of *ca.* 0.7 ppm and 3÷7 ppm was thus estimated for $BMIMPF_6$ 98.5% and 97.0% purity (Figure 1a and 1d), respectively. Interestingly, a significant variation in the chloride amount (*e.g.* 3÷7 ppm for $BMIMPF_6$ 97.0%) was detected in different batches of the same IL purchased in different times. A huge amount of Cl^{-} (*ca.* 0.01 mol dm^{-3}) was estimated in the 98% "BASF-Quality" $BMIMBF_4$ sample by comparing its chloride peak current with the aforementioned calibration plots for $BMIMPF_6$.

On the whole, chloride determination tests in commercial ILs appear to be mandatory in order to avoid unexpected electrochemical behaviour of the medium.

Abatement of the chloride impurities has been performed both on an artificially spiked IL (0.032 M Cl^{-} added to the purest $BMIMPF_6$), and on pristine 98% $BMIMBF_4$ (Figure 2) by constant-potential electrolysis on Ag wire working electrode at 0.2 V (*vs.* SCE) at room temperature. The counter electrode, in the same IL, was inserted in a jacket ending with a porous frit. In fact we had observed that the reduction process at the counter electrode can result in brown colouring which we associated with products of dialkylimidazolium reduction when only low amounts of water are present [6]. However, it is sufficient to insert a few drops of water in the counter electrode compartment to prevent such a process, turning to hydrogen evolution with concurrent acidity consumption, as confirmed by pH measurements. The latter process would be a desirable complementary reaction that could be exploited working in undivided cell in the case of an ionic liquid having acidic impurities concurrently with the chloride ones.

The electrodeposition process is very regular, actually a typical feature of IL media [1,3]. Starting currents depended on the starting chloride concentrations and ionic liquid viscosity (typically 3-9×10^{-4} A) and regularly decreased with decreasing chloride concentration, monitored by periodical scans on the analytical Ag disk electrode, pointing to a first-order kinetics, implying

$$\ln(c/c_0) = \ln(Q/Q_0) = -kt \qquad (3)$$

where Q and Q_0 are the DPV or CV peak charges at time t and $t = 0$ respectively, and a concentration-independent halving time of

$$t_{1/2} = \ln 2/k \qquad (4)$$

Fitting the experimental data with equation (3) yields (a) $k = 5\times10^{-5}$ s^{-1} implying from equation (4) $t_{1/2} = 1.3\times10^{4}$ s in the case of artificially spiked 0.032 M $BMIMPF_6$ and (b) $k = 1.2\times10^{-4}$ s^{-1} and $t_{1/2} = 5.9\times10^{3}$ s in the case of pristine 98% $BMIMBF_4$ (the higher rate constant observed for

$BMIMBF_4$ appearing consistent with lower viscosity).. The charge passed (obtained by integrating the current *vs* time characteristics) appeared to be consistent with the concentration decrease monitored by voltammetric techniques, and the charge passed for chlorides below the CSV limit of detection was only slightly higher than the theoretical one, implying a nearly 100% current efficiency for the desired AgCl formation reaction. In our conditions (implying a working electrode surface/IL, *A/V*, volume ratio of about 1.4-1.6 cm^{-1}) this typically required *ca.* 12 hours, which is however not a problem since the process is well controlled and can safely proceed overnight, just like when performing the first step of bielectrolytic Ag|AgCl electrode preparation according to the classical protocol [7]. In any case, a shorter time could be achieved by increasing the above operating ratio and the stirring rate. The final solution is colourless as at the beginning, its CSV pattern satisfactory, and no significant pH change is observed, provided that the counter electrode is inserted in the separated jacket. The chloride impurities are then removed by simply removing the Ag|AgCl electrode, from which the Ag wire can be easily recovered by sandpaper treatment or immersion in NH_3 solution.

As an example, the DPV and CSV monitoring of the electrolysis concerning pristine 98% $BMIMBF_4$ is provided in Figure 2. In particular DPV was used to follow the first part of the electrolysis, and CSV for the last part, at very low chloride concentrations. Incidentally, it can be observed that, as already mentioned above, the shape of DPV peaks is no more canonical above *ca.* 0.0005 M.

4. Conclusions

Our proposed chloride abatement process affords complete abatement of the chloride impurities in a single step, at room temperature, at very low potentials, with nearly ideal current efficiencies, and with negligible side effects on the electrolyzed IL. The process should be carried out in a divided cell when the water and acidity content is low, but could offer the nice opportunity to simultaneously abate acidic impurities (when present) together with chloride ions. The chloride impurities are thus captured and accumulated on the silver wire and eliminated by simply removing the resulting Ag|AgCl electrode from the solution, with no need of subsequent treatments. Thus our proposed chloride abatement protocol is practically the same as that of the electrolytic preparation of a Ag|AgCl electrode, a very regular and safe process in the IL medium.

Acknowledgements

The financial support of Fondazione Cariplo (grant no. 2011-1851 "Inherently chiral ionic liquids") is gratefully acknowledged.

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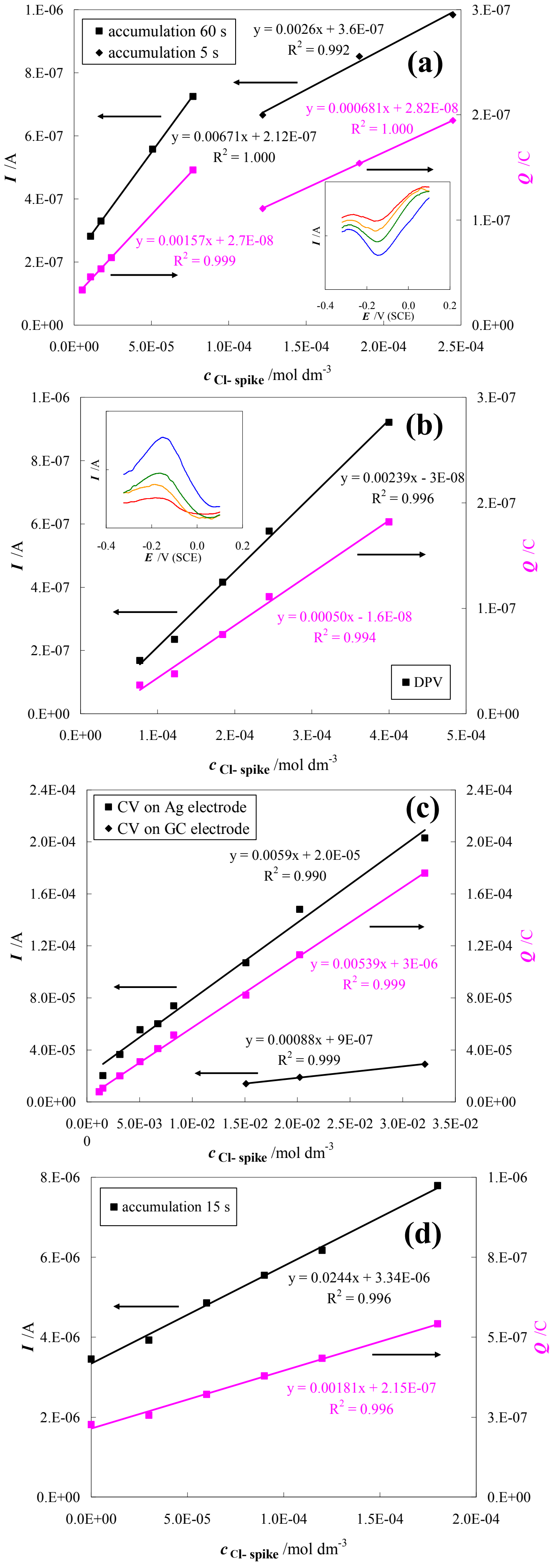

Figure 1. Calibration curves in BMIMPF$_6$ >98.5% for $5\times10^{-6} \div 3.2\times10^{-2}$ mol dm^{-3} added chlorides from a TEACl standard solution, employing different voltammetric techniques at increasing concentrations ((a) CSV; (b) DPV; (c) CV). Insets: examples of CSV (a) and DPV (b) patterns used for the calibration. (d) Standard addition technique plot for commercially available BMIMPF$_6$ >97.0%. Cathodic stripping: 0.4 and 0.1 V (*vs.* SCE) deposition potential for (a) and (d) respectively. Working electrode: Ag disk (0.071 cm^2), GC disk (0.031 cm^2).

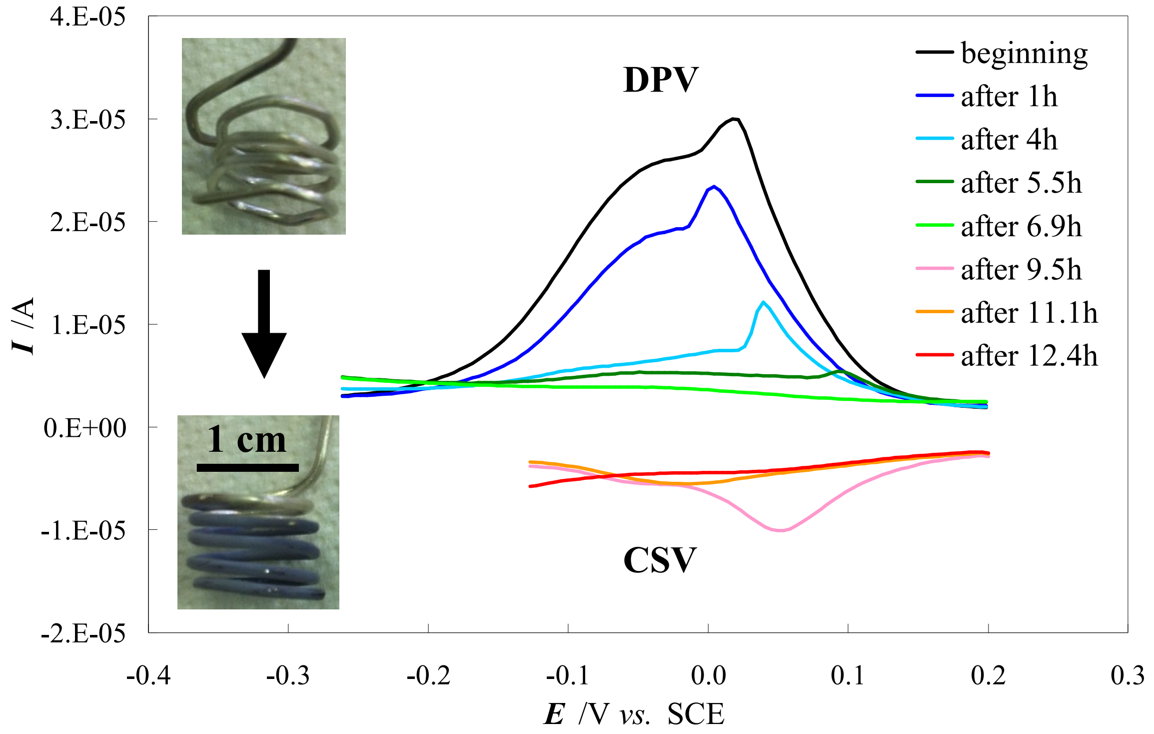

Figure 2. DPV and cathodic stripping voltammograms on Ag disk electrode (0.071 cm^2) recorded during the electrolysis of Cl$^-$ in 3 cm^3 BMIMBF$_4$ using a Ag wire as anode (before and after the electrolysis, in the two pictures). Constant potential electrolysis at 0.2 V (*vs.* SCE). Stripping parameters: 0.2 V (*vs.* SCE) deposition potential, 120 s accumulation time.