Supplementary Information

The Oxidation of 4-Chloroaniline studied by on-line Electrochemistry Electrospray Ionization Mass Spectrometry

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Figure S1. Average background corrected peak intensities (n = 4) as a function of the applied potential E, for **(a)** m/z 217.2, **(b)** m/z 219.2, **(c)** m/z 253.2, **(d)** m/z 128.2 obtained with the conventional ◆, and the modified ■ EC cell, respectively.

Figure S2. Cyclic voltammograms for 1.0 mM 4-CA in Britton-Robinson buffer obtained at pH 2.0 using a scan rate of: 10 mV/s, 125 mV/s, or 250 mV/s.

Experimental.

The two flow-cell set-ups. In the conventional thin-layer flow cell set-up, an Ag/AgCl RE-4 reference electrode (Bioanalytical Systems Inc.) was employed as the reference electrode while the stainless steel block of the flow cell was used as the counter electrode. In this set-up, the working electrode was separated from the counter electrode by a 16 μm spacer gasket. In the modified flow cell set-up, the stainless steel block was instead used as a quasi reference electrode (QRE) while a laboratory made stainless steel electrode, made to fit the reference electrode compartment of the thin-layer flow cell, was used as the counter electrode. This modification of the thin-layer flow cell was made to minimize interferences from the electrochemical reactions occurring at the counter electrode by separating the working electrode from the counter electrode according to common coulometric experimental practice. The potential of the QRE in the 4-CA solutions was found to be +0.246 V with respect to the Ag/AgCl electrode, and all potentials are reported versus the Ag/AgCl reference electrode.

ESI-MS parameters. The fused silica spray capillary entering the mass spectrometer was centered in a stainless steel capillary auxiliary assembly delivering 20 psi of air (zero grade, generated in house) for pneumatically assisted ESI-MS. The flow rate of dry nitrogen (boil off from liquid nitrogen) counter-current curtain gas (heated to 63 °C) was 1.2 l/min over the sampling orifice. The mass spectrometric parameters were as follows: ion spray voltage (ISV) 4500 V, interface plate voltage (IN) 650 V, orifice lens voltage (OR) 50 V, and AC entrance rod (R0) 30 V. Q1 Scans between *m/z* 10-500 (step size 0.1), with a dwell time of 2.5 ms, were recorded in the multi channel acquisition (MCA, summation of 10 scans) mode during 2.08 minutes, after applying potential to the working electrode.

Britton-Robinson buffers. The pH 2.0, 4.0 and 6.0 buffers were freshly prepared as follows: 0.8 M acetic acid (p.a., Merck), 0.7 M phosphoric acid (p.a., Merck), and 0.4 M boric acid (p.a., Merck), were first diluted to obtain a 40 mM solution of all three acids with a pH of 1. The pH was then adjusted employing 0.2 M sodium hydroxide (p.a., Merck) and a 744 pH meter (Metrohm AG, Herisau, Switzerland) to obtain the requested pH 2.0, pH 4.0, and pH 6.0 buffer solutions.

Isotope correction.

One has to consider that Dim_{Ox} (m/z 217) contributes with one of its isotopic peaks to the signal for Dim_{Red} (m/z 219), see **Table S1**, as an example of obtained intensities from EC/ESI-MS when 1.646 V vs. Ag/AgCl was applied. The relative intensities of $C_{12}H_{10}N_2Cl$, for m/z 217 and those of its isotopes are shown in **Table S2**.

Table S1: Mass spectral intensities at 1.646 V vs. Ag/AgCl for the modified EC thin-layer flow cell

m/z	Intensity / cps	Label
217	266400	Int_{217}
218	97600	
219	171600	Int_{219}
220	49600	
221	49200	
222	11600	

Table S2: Theoretical isotopic contribution

m/z	Relative intensity / %
217	100.000
218	14.219
219	32.861
220	4.529
221	0.262
222	0.010

By multiplication of the relative intensity of the third isotopic peak of m/z 217, i.e. m/z 219 (32.861) with the actual intensity of m/z 217, Int_{217} (e.g. 266400 cps), according to equation (S1), the intensity contribution to m/z 219 from m/z 217, $Int(Dim_{Ox})_{219}$, e.g. 87543 cps, was obtained see **Table S3**. Furthermore, by subtracting $Int(Dim_{Ox})_{219}$ from the intensity of 219, Int_{219} (e.g. 171600 cps), the intensity of Dim_{Red}, was obtained using equation (S2), see **Table S4**.

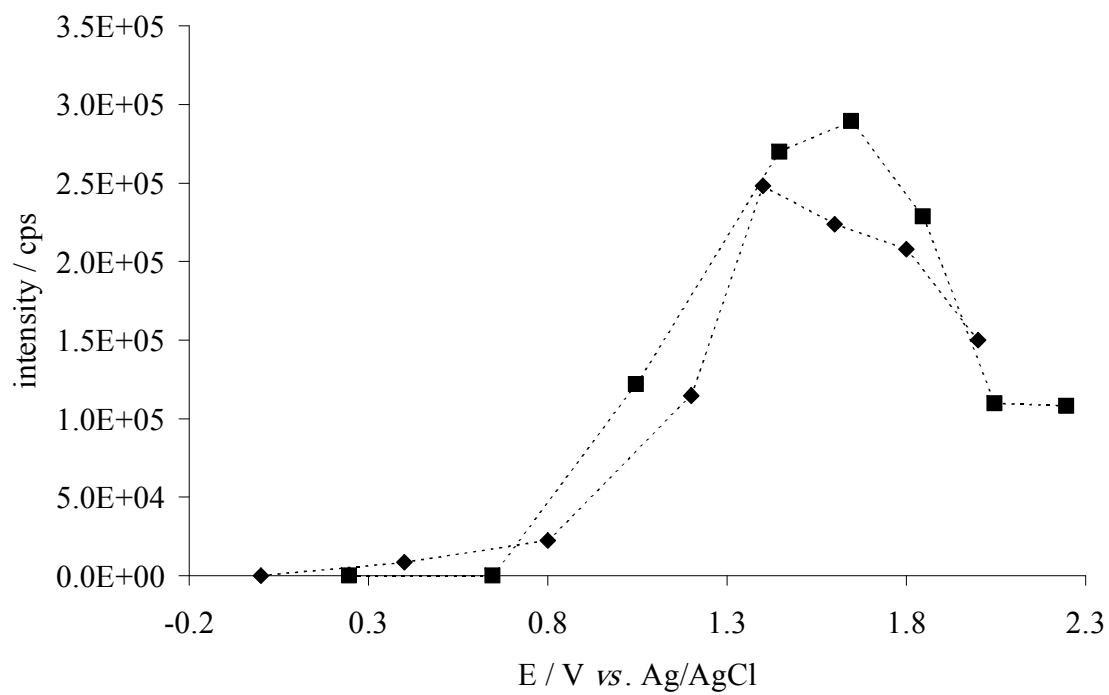$$Int(Dim_{Ox})_{219} = (\text{Relative intensity} / 100) * Int_{217} \qquad (S1)$$

$$Int(Dim_{Red})_{219} = Int_{219} - Int(Dim_{Ox})_{219} \qquad (S2)$$

Table S3: Corrected intensities for Dim_{Ox} (m/z 217) at 1.646 V vs. Ag/AgCl with the modified EC thin-layer flow cell
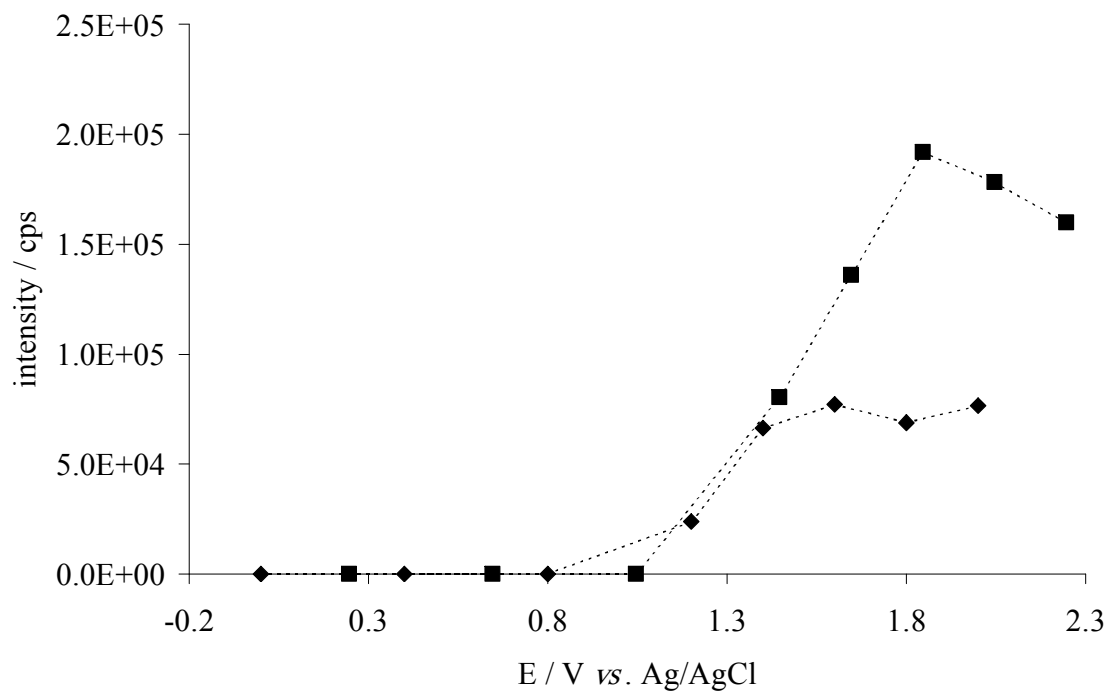
m/z	Label	Corrected intensity / cps
217	Int_{217}	266400
218		
219	$Int(Dim_{Ox})_{219}$	87543
220		
221		
222		

Table S4: Corrected intensities for Dim_{Red} (m/z 219) at 1.646 V vs. Ag/AgCl with the modified EC thin-layer flow cell
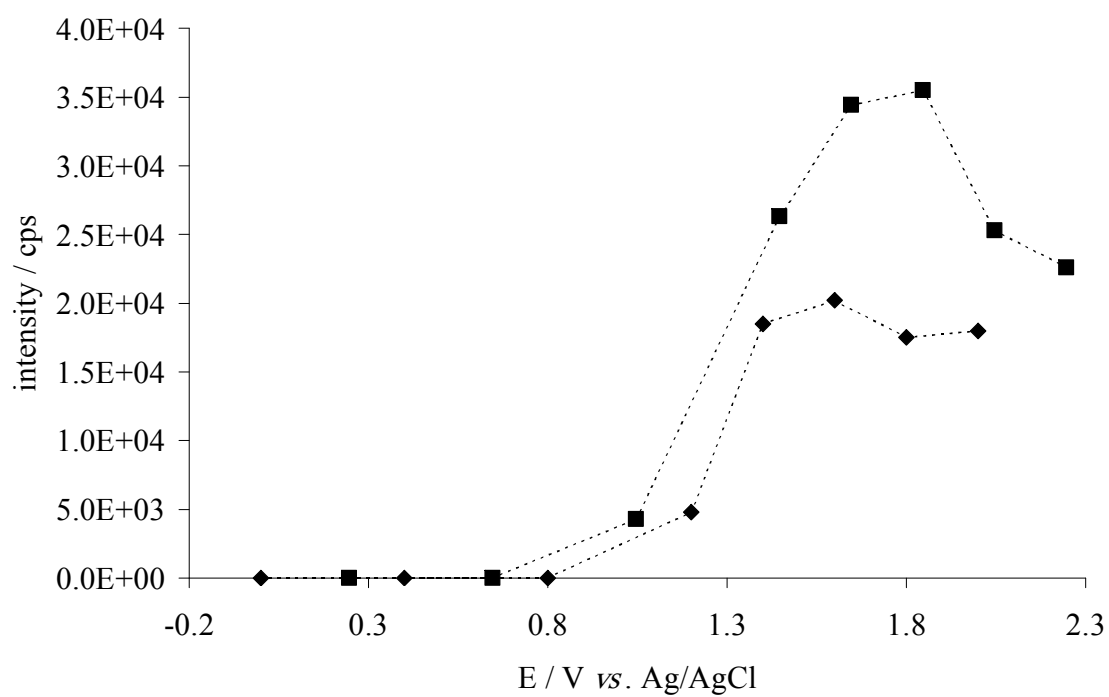
m/z	Label	Corrected intensity / cps
217		
218		
219	$Int(Dim_{Red})_{219}$	84057
220		
221		
222		

(a) *m/z* 217.2, Dim$_{Ox}$

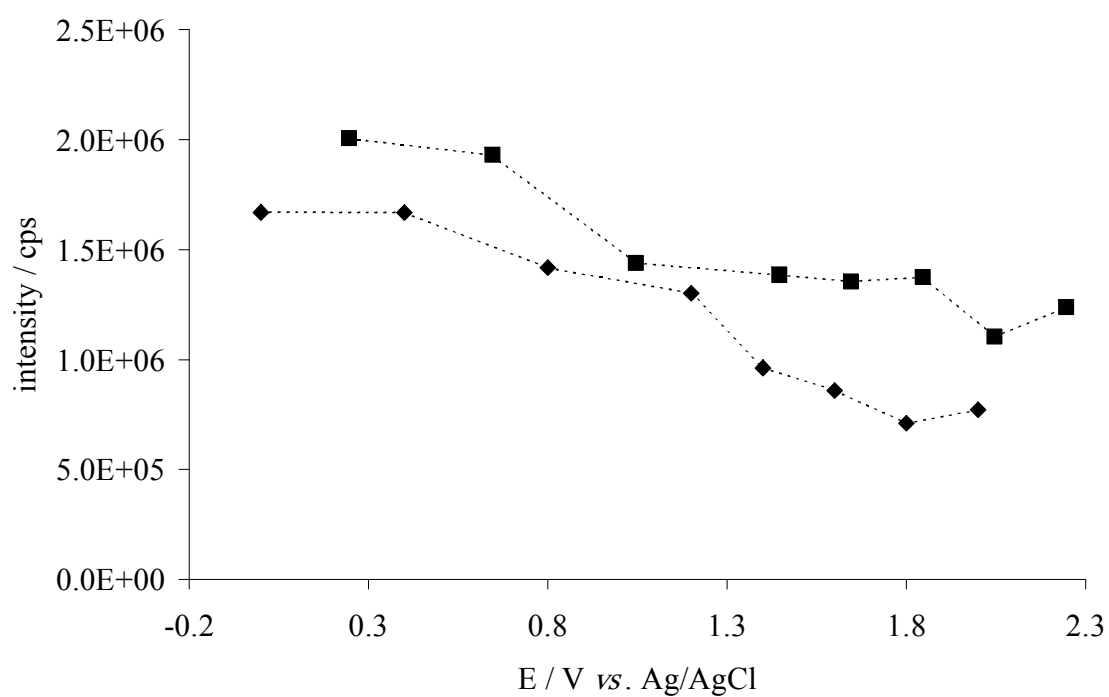(b) *m/z* 219.2, Dim$_{Red}$

(c) *m/z* 253.2, intermediate

(d) *m/z* 128.2, 4-CA

Figure S1

Figure S2