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1	An in situ IR-Vis Sum Frequency Generation Spectroscopy study of
2	cyanide adsorption during zinc electrodeposition
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14 Abstract

15 In this paper, we demonstrate the feasibility of in situ non-linear IR-Vis Sum Frequency Generation (SFG) 16 Spectroscopy investigations at zinc surfaces in electrochemical ambient. We investigated both zinc 17 electrodeposition onto an extraneous electrode and adsorption on polycrystalline zinc. Electrodeposition 18 studies were carried out onto a polycrystalline gold cathode in contact with a Zn-cyanocomplex solution 19 containing free CN⁻, while adsorption studies were carried out on a polycrystalline zinc electrode in contact 20 with a free-CN⁻ solution. In both experiments, we monitored the spectroscopic features associated with the 21 internal stretching of the adsorbed cyanide (ca. 2100 cm⁻¹) that we exploited as local Au and Zn site probes. 22 Spectroelectrochemical results were complemented by cyclic voltammetric measurements. This proof-of-23 principle study is encouraging in the view of more concrete applications regarding additive adsorption at zinc 24 electrodes, aiming at a fundamental understanding of the cycling stability of zinc battery anodes.

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27 **1. Introduction**

28 The electrochemical deposition of reactive metals is nowadays one of the most intensively studied processes 29 in the field of electrochemical energetics, since it is the crucial step of the recharge of many secondary 30 batteries, including metal-air devices. Specifically, interest in Zn electrodeposition from alkaline aqueous 31 electrolytes has been recently revived owing, on the one hand, to the prospective technological importance 32 of rechargeable metal-air batteries [1], and, on the other hand, to serious, so far unsolved, growth instability 33 issues. In fact, the performance of rechargeable zinc-air batteries is largely limited by the low efficiency of 34 the charging stage, due to formation of dendritic zinc structures, which cause short-circuits and capacity 35 losses [2]. Quite a few electrochemical studies have been published in the field of zinc dendrite suppression, 36 mainly based on the use of additives of either organic or inorganic nature (e.g. [3,4]). However, they are 37 mainly empirical investigations aiming at establishing correlations among particular cases, rather than 38 general physico-chemical tools for a knowledge-based control of the process. In order to overcome this gap,

39 fundamental studies are still necessary on the different steps leading to 3D crystallite growth: (i) reduction 40 of the electroactive complexes, (ii) nucleation both on the extraneous cathode substrate and on pre-41 deposited zinc, (iii) subsequent growth, (iv) adsorption of additives and ligands on the dynamically growing 42 zinc layer. Specifically, in situ vibrational spectroscopies can be exploited in order to study the interaction of 43 electrolyte components, such as additive molecules, and electroactive complexes - their ligands, in particular 44 - at the cathodic interface at different stages of the zinc growth. In the case of zinc electrodeposition from 45 alkaline aqueous solutions, to the best of the Authors' knowledge, only one paper has been published on in 46 situ Surface Enhanced Raman Spectroscopy (SERS) study of triethanolamine (TEA) as an additive [5]. 47 Notwithstanding the technical appeal of working with a visible light beam, SERS can be implemented only on 48 nanostructured surfaces that are not always easy to obtain. To overcome this issue, IR-Vis Sum-Frequency 49 Generation Spectroscopy (IR-Vis SFG) can be exploited. IR-Vis SFG is a non-linear spectroscopic technique, 50 which is intrinsically sensitive to interfaces. This property implies that, at variance with FT-IR techniques, SFG 51 does not require the acquisition of differential spectra for potential-dependent in situ work. Of course, the 52 necessity of acquiring successively at least couples of spectra poses stringent requirements on the 53 stationarity of the process being investigated, that can barely be ensured in an electrodeposition experiment. 54 In situ SFG has been used for the investigation of a series of electrodeposition processes of Au, Ag, and Cu-55 based alloys from both aqueous and non-aqueous electrolytes [6,7], but it has never been attempted for that 56 of reactive metals. Nevertheless, publications reporting electrochemical SFG data collected in situ during the 57 corrosion of Co- and W-based alloys [8] bear promise that even a dynamic electrochemical interface can be 58 successfully monitored with this approach. Moreover, literature on ex situ SFG measurements of zinc 59 corrosion brings support to the feasibility of studying the vibrational properties of the zinc/electrolyte 60 interface with this method [9]. In this work we studied zinc electrodeposition on a gold cathode from a Zn(II)-61 cyanocomplex solution with IR-Vis SFG spectroscopy, monitoring cyanide adsorption during 62 electrodeposition. As starting points for the Zn electrodeposition work, we studied the adsorption of CN⁻ in 63 situ on polycrystalline Au and Zn electrodes. For comparison, work on the Au electrode was carried out under 64 the same static and dynamic conditions employed for Zn electrodeposition, both in the absence and in the 65 presence of Zn(II) cyanocomplexes.

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68 2. Methodology

69 2.1 Electrochemical SFG setup

A setup for *in situ* and *operando* electro-chemical and catalytic IR-Vis SFG experiments was developed at the Visible and Infrared Spectroscopy Laboratory at the Physics Department of the University of Trieste [10]. The experiments take place in a dedicated three electrode electrochemical cell – consisting in a modification of the concept described in [11] – assembled on a holder, inside a black box, and controlled by a potentiostat (AMEL 551).

The body of the electrochemical cell for in situ SFG is made of polyvinyl chloride (PVC) and consists of different 75 76 parts (see Figure 1): the electrolyte compartment, equipped with the appropriate electrical contacts for the 77 working- (WE, 1), reference- (RE, 3) and counter-electrodes (CE, 4), a sample compartment (6), a vacuum 78 pump tube to hold the WE in position by suction (2), and a calcium fluoride (CaF₂) prism (5). A copper screw 79 present in the compartment (1) provides the electric contact of the WE with the potentiostat connections. 80 The copper screw does not touch directly the WE, but it is connected to it by means of a helical platinum 81 wire, reaching the bottom of the WE through an evacuated perforated plastic tube, terminated with an O-82 ring seat, that is sealed by the WE itself, held in place by depression. The copper screw also allows the fine 83 tuning of the WE distance with respect to the prism surface, in order to control the electrolyte thickness 84 required for IR transmission. An Ag/AgCl RE is fixed in its compartment by means of a screw. The CE is a

wound platinum wire, exhibiting a surface area of 2 cm^2 in contact with the electrolyte. The prism on the one 85 86 hand seals the cell leaving an electrolyte gap of appropriate thickness and, on the other hand, drives the 87 impinging Vis and IR beams to the WE surface and channels the resulting SFG beam to the detector. 88 Moreover, two holes have been drilled into the prism away from the optical path of the three light beams to 89 enable experiments in which the electrolyte can be continuously circulated by means of a peristaltic pump. 90 This capability of the cell was not exploited in the present investigation. The cell holder is equipped with 91 micrometric screws, allowing fine positioning along 6 degrees of freedom, in order to optimize the alignment 92 of the WE with the light beams. The holder allows the following movements: (i) in-plane along the x and y 93 directions, parallel to the sample surface; (ii) vertical, in the z direction, normal to the sample surface; (iii) tilt 94 around the x and y axes; (iv) azimuth around z.Potentiostatic tests in the SFG cell compared with similar ones 95 carried out in a conventional, optimized three-electrode cell have shown that the ohmic drop is negligible in 96 the current-density range of interest for electrodeposition work.

97 The box that encloses the electrochemical cell possesses a system of lenses, which drives the impinging IR 98 and Vis beams to the sample surface at 55° and 60° with respect to the surface normal, respectively, with the 99 desired polarization. The lenses drive the resultant SFG beam to the monochromator (MS2001) and to the 100 photomultiplier tube detection system (Hamamatsu R7899). In the present study, all spectra were collected 101 in the ppp polarization configuration (SFG-visible-infrared). The visible beam (532 nm) and the tuneable IR 102 beam (1000-4500 cm⁻¹) used for the SFG experiments are generated by means of an EKSPLA setup described 103 in [10]. Data acquisition and instrument control are performed remotely via custom LabVIEW software 104 interfaces.

105

106 2.2 Data processing

107 SFG spectra were analysed by least-squares fitting to a literature expression of the non-linear second order 108 susceptibility (Eq. 1) [12], after normalization to the impinging visible and IR intensities, in order to remove 109 the modulations caused by the laser instability and intrinsic to the IR generation process. In the case of raw 110 spectra exhibiting a tilted background, we removed the slope and set the background level to its average. 111 The non-resonant background originates indeed from the combination of the nonlinear responses of free 112 and bound electrons in the metal [13-15] associated with plasmonic resonances, especially in the case of 113 electrodeposition, that intrinsically generates nanocrystals [6]. This signal does not vary significantly with the 114 IR frequency range of the measurements- (less than 200 cm⁻¹), and can therefore be assumed as constant 115 with reasonable accuracy. Indeed, for gold it is found to vary of a factor of three moving from 400 to 700 nm 116 the visible excitation wavelength (i.e. spanning about 10^4 cm⁻¹) [13-15], The deconvolution yielding the SFG 117 data plots is reported in [10]

118

119
$$\frac{I^{SFG}(\omega_{IR})}{I_{vis}I_{IR}(\omega_{IR})} \propto \left| A^{(NR)} + \sum_{\upsilon} \frac{A_{\upsilon}^{(R)} e^{i\Delta\phi_{\upsilon}}}{\Omega_{\upsilon} - i\Gamma_{\upsilon} - \omega_{IR}} \right|^2 (1)$$

120

Briefly, $A^{(NR)}$ and $A_{\upsilon}^{(R)}$ are the non-resonant and v_{th}-resonant amplitudes, respectively; $\Delta \varphi_{\upsilon}$ is the phase difference between the v_{th}-resonant and non-resonant signals; Ω_{υ} is the energy position of the line and Γ_{υ} is the resonance Lorentzian broadening, which is related to the decoherence time of the excited state. A Gaussian broadening was also considered by means of a convolution of the lineshape, mainly accounting for the inhomogeneity contributions in the adsorbed species population [16]. In this paper, the normalized SFG spectra (black dotted lines) are presented together with the corresponding best-fit function (red line), the deconvoluted components (color-filled profiles), and the residual (dark-yellow filled profiles).

129 2.3 Sample preparation

130 In this study we employed Au and Zn WEs in the form of discs. The former metal was used as the a cathode 131 for both adsorption and Zn electrodeposition from an aqueous cyanide solution. Zn discs were exploited 132 instead for the adsorption studies. The polycrystalline gold WE used for the zinc electrodeposition studies (8 mm diameter) was cleaned with the following procedure before each experiment: (i) mechanical polishing 133 134 with abrasive paper down to 1200 grit and with 1 µm diamond paste; (ii) immersion for 5 min in a 135 concentrated solution of nitric acid (69.5% HNO₃) to remove organic contaminants; (iii) rinsing with milli-Q 136 water; (iv) annealing in a butane flame to red colour, followed by quenching with milli-Q water (the flaming-137 quenching sequence was repeated at least three times); (v) the cleaned WE was protected with a drop of 138 ultra-pure water and transferred to the electrochemical cell without direct exposure to air. The 139 polycrystalline zinc WE (9 mm diameter) was mechanically polished as described above and electrochemically 140 cleaned in situ in the measurement cell, potentiostatically, in the range of the hydrogen evolution reaction 141 (HER) for about 20 minutes.

142

143 2.4 Electrolytes

We employed free CN⁻-based aqueous electrolytes: a Zn(II)-cyanocomplex bath containing free CN⁻ for the electrodeposition studies and a CN⁻ solution for adsorption investigations on Au and Zn. The CN⁻ solutions were obtained by dissolving 25 mM KCN and 0.1 M NaClO₄ in milli-Q water or by prolonged cathodic reaction of 25 mM 4-cyanopyridine in the same perchlorate supporting electrolyte [17]. The cyanocomplex bath was obtained by dissolving 5 mM ZnO to the KCN solution, whereby the Zn(II) cyanocomplex forms spontaneously.

150

151 2.5 Electrochemical measurements

152 Cyclic voltammetry (CV) experiments were performed with polycrystalline Au and Zn electrodes in contact 153 with the solutions employed for SFG measurements and, in addition, with the NaClO₄ 0.1M supporting 154 electrolyte, for comparison. Moreover, calibration runs were performed also with HClO₄ 0.1M: but are not 155 reported for brevity. The working electrodes and their preparation methods were the same used for SFG. 156 The measurements were carried out in a conventional three-electrode cell, equipped with an Au wire 157 counter-electrode and an Ag/AgCl (KCl 3M) reference electrode. All potentials in this work are reported on 158 the Ag/AgCl scale. In order to highlight small voltammetric features in the cathodic range, the solutions were 159 deaerated by N_2 bubbling before the measurement and an N_2 blanket was kept during the CV measurement. 160 The scan rate was 100 mV s⁻¹.

161

162 2.6 Experiments design

163 The ultimate goal of this investigation is to achieve a better understanding at the molecular level of the zinc 164 growth process by *in situ* monitoring of the adsorption of CN⁻, the cyanocomplex ligand, present in the bath 165 in excess, as customary in alkaline metal plating baths. In the cyanoalkaline Zn bath chemistry, CN⁻ acts at the 166 same time as the ligand of the metal electroactive species and as a probe-molecule of the dynamic state of 167 the growing metal surface. In analogy with our previous in situ SERS study of a similar system [5], the experiment was performed starting with a clean polycrystalline gold surface (Aupoly) immersed in a Zn-168 169 cyanocomplex solution containing free CN⁻ (see Section 2.4), from which zinc can be deposited by means of 170 an appropriate cathodic bias. Even though the aim of our study is to follow the zinc growth, for reference – 171 after the protocol, developed in [5] – we also investigated CN⁻ adsorption on the Au cathode from the Zn(II)-172 free solution. The electrochemical behaviour of this system is well known in the literature [18] and represents 173 the benchmark against which the zinc growth process was studied, by contacting the Au cathode with the 174 Zn(II)-cyanocomplex bath and electrodepositing Zn by means of an applied bias. Both experiments were 175 carried out at three applied bias values: -700, -920 and -990 mV. We chose these potentials because they are 176 related to three specific electrochemical conditions with respect to the Zn electrodeposition process. At -700 177 mV electrodeposition does not occur, while at -920 mV electrodeposition takes place at a low rate, and at -178 990 mV electrodeposition runs at a relatively high rate, compared with our data collection time: indeed, we 179 chose those specific deposition potentials in order to define growth speeds that are compatible with the 180 acquisition rate of the spectrometer (ca. 15 min per spectrum). SFG spectra were collected, at each potential, in the 2030 ÷ 2170 cm⁻¹ wavenumber range, associated with the C=N internal stretching mode. The 181 182 experimental protocol consisted in starting with a freshly flame-annealed Au surface, applying a 183 potentiostatic polarization of -700 mV for ca. 30 min, and then stepping to a selected more cathodic potential 184 to record the SFG spectra sequentially in time. CN⁻ adsorption onto bulk polycrystalline Zn was studied at 185 OCP (-830 mV) and at -1250 mV. SFG spectra were collected at each potential in the 2030 ÷ 2250 cm⁻¹ 186 wavenumber range.

- 187
- 188
- 189 **3. Results**

190 **3.1 Cyclic voltammetry**

191 Figure 2 reports the CV curves recorded with a polycrystalline Au electrode in contact with (1) the pure 192 supporting electrolyte 0.1 M NaClO₄), (2) 0.1 M NaClO₄ + 25 mM KCN, and (3) 0.1 M NaClO₄ + 25 mM KCN + 193 5 mM ZnO. The black curves show the electrochemical behaviour of Au and span both cathodic and anodic 194 conditions, while the red curves focus on the potential range specifically investigated in the SFG experiments. 195 The voltammogram recorded in the pure supporting electrolyte (curve (1)) exhibits an evident 196 electrochemical window that spans the potential range limited by the features A, Ba, and Bc. The former 197 corresponds to the onset of the hydrogen evolution reaction, the latter two to the formation (anodic branch: 198 B_a) and the reduction (cathodic branch: B_c) of an Au oxide film, respectively. In the double-layer charging 199 region, small features can be noticed, corresponding to well-known potential-dependent restructuring of the 200 Au surface [19, 20]. At higher anodic potentials the oxygen evolution reaction onset can be noticed (feature 201 C). Moreover, a slight oxygen reduction reaction background is observed for potentials more cathodic than ca. -0.5 V. The addition of KCN (curve (2)) leads to the disappearance of features B and to the growth of two 202 203 different cathodic features (D_c, E_c) and three new anodic ones (D_{a1}, D_{a2}, E_a). D_{a1} and D_{a2} correspond to the 204 formation of Au(I) cyanocomplexes, the former peak is due to the growth a pseudo-passivating film of 205 insoluble AuCN, while the latter shoulder correlates with gold dissolution in the form of soluble Au(CN) $_2$ ⁻. On 206 the cathodic side, peak D_c correlates to the reduction of the Au(I) film. The nature of peak E_c is slightly 207 different, depending on whether the anodic terminal potential (ATP) reaches the Au oxidation range or not. 208 In the former case, since no $Au(CN)_2^-$ is present in the solution, E_c corresponds merely to cathodic desorption 209 of CN⁻ from the metallic Au surface. In the latter case, in which the peak is also more pronounced and 210 broader, desorption of CN⁻ takes place together with the faradaic reaction of Au(CN)₂⁻reduction to elemental 211 Au (equilibrium potential: -820 mV). Finally, peak E_a denotes CN^- adsorption onto the metallic Au surface. 212 More details on the electrochemistry of the Au/CN⁻ system can be found in already published literature [6, 213 21]. The presence of both CN^- and Zn^{2+} (curve (3)) leaves peaks D_c and D_{a2} essentially unmodified, while peak 214 D_{a1} splits into two, probably owing to the formation of a monolayer of Zn-alloyed Au. This phenomenon is 215 known in perchlorate solutions with a range of anions [22, 23], but the specific case of CN⁻ has not been 216 addressed in the literature yet. Nevertheless, the formation of a second peak, ca. 0.25 V more anodic that 217 the Au-oxidation one, is compatible with a process of this type. Peak E_c is still present and again a dependence 218 in peak position and shape on the ATP is found, as in the case of the solution containing only CN⁻. This peak 219 is modified by the presence of Zn²⁺, owing to the fact that Zn deposition from uncomplexed Zn²⁺ occurs in 220 this potential range, as also witnessed by the formation of an evident Zn layer by potentiostatic deposition in this potential range. This is further confirmed by shifting the cathodic terminal voltage to -1.5 V, where Zn electrodeposition from complexed Zn²⁺ occurs (see inset of Figure 2). It can be noticed that the cathodic branch of the voltammogram is not modified above -1.2 V, but in the anodic one new anodic stripping features appear (F) due to previous bulk Zn deposition from the more abundant complexes.

225

226 In Figure 3 we show the CVs measured with a polycrystalline Zn electrode in contact with (1) the pure 227 supporting electrolyte 0.1 M NaClO₄, and (2) 0.1 M NaClO₄ + 25 mM KCN. The black lines describe the 228 behaviour of Zn in the potential range encompassing Zn corrosion and HER, while the red curves correspond 229 to the conditions employed for the SFG experiments. The CV recorded with the pure supporting electrolyte 230 in the wider potential window exhibits a couple of cathodic peaks (C_1, C_2) and an anodic one (A), in addition 231 to Tafel-type current density growth regions corresponding to Zn corrosion (B) and HER (D). The anodic peak 232 A is suppressed if the CTP (cathodic terminal potential) is set to -1.25 V. Coherently with the literature [24], 233 the peaks can be assigned to the corresponding processes. In the specific: (A) passivation of the Zn film by ZnO precipitation; (B) transpassive corrosion of Zn, releasing Zn²⁺ into the electrolyte; (C₁): reduction of Zn²⁺ 234 235 ions in solution; (C_2): reduction of the ZnO film. The reason why peak A is suppressed when the cathodic 236 potential is reversed at -1.25 V, is that the ZnO film is still stable in the relevant potential range and only 237 transpassive processes can take place. The same features are found also in the presence of CN⁻ in solution, 238 but they are less evident in the latter case, witnessing anion adsorption in the whole investigated potential 239 range. To the best of the authors' knowledge, no literature has been published regarding the interaction of 240 CN⁻ with Zn surfaces: a hint to corrosion protection afforded by CN⁻ can be gleaned from a patent addressing 241 the synergy of cyanide and Hg as corrosion inhibitors for Zn anodes [25].

242

243 **3.2 SFG investigation of CN⁻ adsorption at a polycrystalline gold surface**

244 In Figure 4 we show the spectra collected as a function of time at V_{bias} in the range -700÷-990 mV. Panels (a) and (b) report time series of spectra measured at -920 and -990 mV respectively. The measurements at each 245 246 potential were recorded starting from a freshly prepared Au surface. The potential was initially set to -700 247 mV for ca. 30 min (top spectrum in panel (a)), yielding stationary spectroscopic conditions, and then it was 248 stepped at the selected value. Time zero corresponds with the application of the latter bias step. All the 249 spectra of both series could be fitted with a single vibronic resonance, assigned to the internal stretching of 250 C=N adsorbed via the carbon atom. At -700 mV the resonance is positioned at $2110 \div 2111$ cm⁻¹ and, on the 251 basis of the literature ([26] and references therein), can be associated with CN⁻ adsorbed on a partially 252 oxidized gold surface resulting from exposure of Au to the aerated CN⁻ solution [18]. Upon stepping the bias 253 to -920 and -990 mV the resonance shifts to 2101.0 \pm 0.5 and at 2085.8 \pm 0.5 cm⁻¹, respectively. These values 254 correspond to the internal stretching mode of the cyanide adsorbed on fully metallic gold and are coherent 255 with the Stark shift values reported in the literature [6, 18]. This spectroscopic scenario is also in line with the 256 stabilization of metallic Au promoted by the cathodic potentials lower than -700 mV. The time evolution of 257 the lineshape parameters for the spectra of Figure 4 is plotted in Figure 5. Immediately after switching the 258 potential to -920 mV, the spectra show an evident redshift with respect to the -700 mV bias (Figure 4a and 259 top of Figure 5a). The redshift becomes larger as a function of time and it is accompanied by a reduction of 260 the peak amplitude. The time and bias spectral evolution is in perfect agreement with the progressive 261 reduction of the Au surface caused by the applied cathodic potential: related mechanistic details can be 262 found in [26]. A progressive decrease of the oxidative adsorption leads to the reduction of the intensity of 263 both the resonant (bottom plot of Figure 5a) and nonresonant amplitudes (bottom plot of Figure 5b). The 264 Gaussian broadening, associated with the surface inhomogeneity, (top plot of Figure 5b) is essentially 265 constant, thus excluding an evolution in time of the surface homogeneity or roughness at the atomic scale in 266 this case. As hinted-at above, in the present case, in which Au reduction from an adsorbed Au(I) 267 cyanocomplex takes place [26], the non-resonant background is expected to exhibit a significant contribution 268 from the electronic excitations at the metal surface caused by the interaction of the gold sample with the Vis 269 beam [13-15]. Thus, during the transient stage, a modification of the surface electronic properties occurs and

- is observed *in situ*: this optical response is in matching with the reduction of the Au surface, caused by the applied cathodic polarization. Panels (c) and (d) of Figure 5 report the corresponding spectral time-evolution for the time series collected at $V_{bias} = -990$ mV. In this case – corresponding to a higher cathodic bias and
- 273 consequently higher Au-reduction rate the evolution of the system is notably faster and, when compared
- with the spectral acquisition time, so that only a very limited cathodic peak shift can be observed in this time series. Stationary conditions are essentially attained already after the collection of the first few spectra.
- 276

277 **3.3 SFG** investigation of CN⁻ adsorption at a growing Zn surface during electrodeposition

Similar experiments have been performed with Zn(II) cyanocomplexes present in the solution. Figure 6 reports spectra collected in the presence of Zn(II) in the potential range -700÷-990 mV, as a function of time. The spectroscopic scenario at -700 mV replicates that found in the absence of Zn(II), with negligible changes in the fit parameters: this is quite reasonable because on the one hand Zn(II) cannot react at this potential and, on the other hand, adsorption of free CN^- is expected to be much stronger than that of the cyanocomplex.

284 The time evolution of the fit parameters of SFG spectra collected in situ during the Zn electrodeposition 285 process is reported in Figure 7 for the two experiments performed at -920 mV (0.15 \pm 0.018 μ A cm⁻²) and -286 990 mV ($12 \pm 4 \,\mu$ A cm⁻²). Of course, owing to the phase-formation process that is active at both potentials, 287 increasing electrodeposition times at higher cathodic polarizations correspond to thicker Zn layers. In Figure 288 6 we also plot, in addition to the complete time series, the deconvolution of selected, representative spectra. 289 The first result of the spectroscopic investigation is that all spectra, of both series, could be deconvoluted 290 with two resonances constantly centred at 2099 and 2081 cm⁻¹ that can be associated with the CN⁻/Au and 291 CN⁻/Zn species, respectively. So, while in the absence of Zn a single resonance shifting in position with time 292 was observed, when Zn deposition goes on we can distinguish two spectral contributions, associated with 293 CN⁻ adsorbed on the residual uncovered Au areas and at the Zn growing islands, partially covering the 294 cathode. The resonance width associated with the decoherence time was kept fixed at 5.9 cm⁻¹, the value 295 found in the experiments described in Section 3.2. Indeed, in both cases the vibronic features are associated 296 with the cyanide species, and it is reasonable to assume a similar coherent resonance lifetime in a first 297 approximation in order to limit the number of degrees of freedom in the fitting procedure. Panel (a) of Figure 298 7 reports the time evolution of the phase and amplitude parameters for both resonances measured at -920 299 mV. The resonant amplitude of the CN⁻/Au species is evidently a decreasing function of time, suggesting a 300 progressive decrease of the bare Au area due to the growth of Zn islands. Of course, CN⁻/Zn species are 301 absent at the beginning of the Zn-growth experiment, starting with a clean Au cathode. With the progressive 302 deposition of Zn, the resonance amplitude associated with the CN⁻/Zn species initially increases, and, after 303 ca. 100 min of electrodeposition, it starts to decrease, indicating that CN⁻ tends to undergo cathodic 304 desorption from thicker Zn layers. Electrodeposited Zn also clearly impacts the resonance phases. At the 305 beginning of the experiment, where essentially only the CN⁻/Au species is present, the phase corresponds to 306 the value found in the absence of Zn(II) in solution (see Section 3.1), typical of destructive interference with 307 the non-resonant background, as expected for CN/Au layers. The progressive Zn growth gives rise to an initial, 308 progressive formation of an Au-Zn surface alloy [5], followed by the evolution of a thicker, bulk Zn layer. 309 Correspondingly, the relative phase value of the resonances increases, yielding constructive interference with 310 the non-resonant background. This reflects in the different absorption properties of Au and Zn for the visible 311 light, associated with very different electronic density of states close to the Fermi level. In particular, we 312 observe that the phase evolution of the CN/Au and CN/Zn resonances is close to identical in the transition 313 period corresponding to progressive Zn buildup (ca. 50-190 min). In this time interval, we observe an almost 314 constant dephasing of ca. 90-100°, suggesting that such phase evolution is controlled by the NR term, which 315 consists in a mixture of contributions from Au and Zn. In the specific, the phase difference between the 316 resonance terms remains constant, thus pointing to an unchanged CN bonding geometry, while both values 317 shift progressively with respect to the NR phase term. The latter phenomenon reasonably indicates therefore

that the electronic configuration of the electrode is progressively changing with the Zn deposition and growth.

320

Then, if we concentrate on zone II, it seems to me that the phase evolution is rather identical for both resonances. In other words, the dephasing between CN/Au and CN/Zn seems rather constant (or close to that) around 90-100°. So that would mean that 1) there is a constant dephasing between CN on Zn and Au and 2) the phase evolution is solely due to the nonresonant term, which consists of a mixture of NR from gold and NR from Zn.

326

327 The Gaussian width and the non-resonant amplitude, obtained from spectra measured at -920 mV, are shown 328 as a function of time in Panel (b) of Figure 7. Progressive modifications of the surface structure due to the 329 deposition of zinc, reaching stationary conditions after ca. 100 min, are compatible with the observed slight 330 time-dependence of the Gaussian broadening, indicating increasing chemical and geometric inhomogeneity, 331 and roughness of the electrode surface. The non-resonant background progressively decreases with time, 332 since the deposited zinc induces modifications in the electronic properties of the surface. In the time series 333 collected at V_{bias} = -990 mV (Figure 7b), where the Zn growth rate is ca. three times higher than at -920 mV, 334 only one resonance could be resolved, that almost vanishes after ca. 150 min of electrodeposition. This is in 335 agreement with the experiment performed at -920 mV, since CN⁻ tends to desorb cathodically from thick Zn 336 layers. The cathodic desorption potential of CN⁻ [20] and of cyanocomplexes [6] depends on the electronic 337 structure of the adsorption bond that is in turn influenced by the metal substrate. Dedicated experiments 338 and quantum-chemical computations would be needed for a better grasp over this process and are however 339 beyond the scope of the present paper. Nevertheless, we can still say that anticipation of CN⁻ desorption 340 from Zn with respect to Au is expected owing to the lower electrochemical nobility of the former metal [27]. 341 In the fitting procedure, the Gaussian width and phase value were fixed since already after 40 min the 342 resonance almost vanished. Instead, we kept monitoring the NR and resonant amplitudes. The increase of 343 the NR background is evident, suggesting a rearrangement of the surface where the growing Zn layers and 344 residual bare gold terminations coexist.

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346 3.4 SFG investigation of CN⁻ adsorption at a polycrystalline zinc surface

347 Figure 8 shows the SFG spectra collected at OCP (-830 mV) and at -1.25 V (0.43 \pm 0.09 mA cm⁻²) at the 348 interface between a bulk Zn electrode and the free- CN^{-} solution. In both cases, a resonance was clearly distinguished at 2101 ± 3 and 2104 ± 5 cm⁻¹, respectively, associated with the C=N internal stretching of 349 350 cyanide adsorbed through the carbon atom. The relatively wide confidence intervals take origin from the 351 rather low signal-to-noise ratio in the spectra due to the large amplitude of the non-resonant background 352 and the low resonant signal from the low density adsorbate layer. This does not allow to distinguish the two 353 peak positions and, in particular, to assess a Stark tuning, which is in any case expected to be limited owing 354 to the weak interaction of the adsorbate with the reacting electrodic surface. Coherently with the analysis of 355 the case of cyanide adsorption on Au, the HWHM Γ was fixed to 5.9 cm⁻¹, while the other parameters were 356 optimized. Owing to the relatively low signal-to-noise ratio – due to the low surface coverage with adsorbed 357 CN⁻ for the reasons mentioned at the end of Section 3.2-, the quantitative value of the fit parameters is 358 limited, and only the estimate of the resonance position can be rigorously trusted. Nevertheless, the 359 presence of the $v(CN_{ads})$ signal is evident already by inspection of the bare data and, from the point of view 360 of in situ spectroscopy at the surface of a reactive metal, this fact is a notable achievement in its own right, 361 since it proves the presence of the adsorbate at relatively high cathodic polarizations. In the electrolyte used 362 for this study, OCP is a corrosion condition for Zn and the corresponding electrodic potential is rather

negative. Moreover, the potential required to achieve a cathodic polarization is very close to the desorption potential of CN^- from an Au surface. Still, in the absence of cathodic release of ligands due to the electrodeposition process, spectra of adsorbed CN^- can be measured. This result is therefore promising in the view of a systematic *in situ* SFG investigation of Zn battery anodes during both charge and discharge processes.

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370 4. Conclusions

The aim of this paper is to prove the feasibility of *in situ* electrochemical non-linear IR-Vis Sum Frequency Generation Spectroscopy (SFG) during Zn electrodeposition. In fact, SFG is highly appealing to investigate adsorption phases under electrochemical control and it is well known that adsorption of additives at the zinc anode surface is crucial, though poorly understood, for controlling the cycling stability of rechargeable zinc batteries [28]. The first demonstration has been based on the Zn/CN⁻ model system that, though not directly in connection with battery-related issues, nevertheless has a solid practical background in the field of alkaline zinc plating.

378 Specifically, we investigated the zinc electrodeposition process on a polycrystalline gold disc in contact with 379 a Zn-cyanocomplex bath, by monitoring the adsorption of the CN⁻ ion. This study was carried on at three 380 representative biases. (i) At -700 mV, where electrodeposition does not occur, one resonance is found both 381 in the absence and in the presence of dissolved Zn(II) cyanocomplexes. (ii) At -920 mV, a zinc layer was 382 deposited, giving rise to a surface Au-Zn alloy and, in correspondence, the SFG spectra were deconvoluted 383 with two resonances, associated with the cyanide species adsorbed both on metallic gold and at zinc sites. 384 (iii) At -990 mV, a thicker zinc layer was deposited and only one resonance could be resolved, associated with 385 cyanide adsorbed at metallic zinc sites. This resonance progressively looses intensity with time, suggesting 386 cathodic desorption induced by the deposited zinc layer, anticipated in potential with respect to a bare Au 387 surface.

Cyanide adsorption onto a polycrystalline zinc electrode in contact with a free-CN⁻ based aqueous solution was studied at OCP (-830 mV) and -1250 mV. Due to the surface reactivity of zinc in these conditions, our data showed a low signal-to-noise ratio that nevertheless allowed to clearly resolve a single resonance, associated with adsorbed CN⁻.

These results demonstrate the possibility of employing in *situ* SFG to monitor adsorption processes at zinc electrodes with running cathodic and anodic faradaic reactions, thus paving the way to the molecular-level study of practically relevant modifications occurring at the zinc anodes during charge-discharge cycling of highly prospective zinc-based batteries.

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- Figure 1 a) Photograph of the cell assembled on the sample holder. 1) WE electrode contact cavity. 2) Vacuum pump tube. 3) RE electrode contact cavity. 4) AUX electrode contact. 5) CaF_2 prism. 6) Electrolyte
- 440 cavity. The sample is also visible. b) Scheme of the cell. Numeration is the same as a).
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Figure 2 - CV for polycrystalline Au electrode in contact with the following aqueous solution: (1) 0.1 M NaClO₄; (2) 0.1 NaClO₄, 25 mM KCN; (3) 0.1 NaClO₄, mM KCN, mM ZnO. Red curves indicate the potential range specifically investigated in the SFG experiments, black curves indicate the electrochemical behaviour of Au spanning both cathodic and anodic conditions. Inset: same conditions as in plot (3) of Panel (a), but with wider cathodic range (blue curve). Scan rate: 100 mV s⁻¹.



Figure 3 - CV for polycrystalline Zn electrode in contact with the following aqueous solution: (1) 0.1 M NaClO4;
(2) 0.1 NaClO4, 25 mM KCN. Scan rate: 100 mV s⁻¹. Red curves indicate the potential range specifically
investigated in the SFG experiments, black curves indicate the electrochemical behaviour of Au spanning
both cathodic and anodic conditions.







Figure 4 – SFG spectra in the CN⁻ stretching region collected at V_{bias} = −920 (Panel (a)) and -990 (Panel (b)) mV vs Ag/AgCl as function of time. At the top of Panel (a) we report a representative spectrum measured at -700 mV vs Ag/AgCI: in these conditions no evolution of the spectra was observed with time. At the top of Panel (b), for reference, we show the last spectrum measured at -920 mV vs Ag/AgCl (169 min after the application of bias). The best-fit (red line) of the data (black, dotted line) is shown for each spectrum.



Figure 5 - Resonant position shift ($\Delta v = v(t)-v_0$), resonant amplitude, gaussian parameter (G) and non-resonant amplitude (NR) associated with the corresponding to CN⁻ adsorbed on Au as a function of time obtained by fitting the spectra measured at -920 (Panels (a, b)) and -990 mV vs Ag/AgCl (Panels (c, d)).



SFG Intensity / a.u.



SFG Intensity / a.u.



Figure 6 – SFG spectra in the CN⁻ stretching region collected at $V_{\text{bias}} = -700$, -920 mV (Panel (a) and -990 mV(Panel (b)) vs Ag/AgCl as a function of time. The best-fit (red line) of the data (dotted line) is shown. On the right side, three illustrative spectra of the series are depicted (black dotted lines), together with the related best-fit (red line), the deconvoluted components (color-filled profiles) and the residual (dark-yellow filled profile).

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Figure 7 - Phase (ϕ), resonant amplitude, gaussian parameter (G) and non-resonant amplitude (NR) associated with adsorbed CN⁻ resonances as a function of time, obtained by fitting the spectra measured at -920 mV vs Ag/AgCl (Panels (a, b)) and -990 mV vs Ag/AgCl (Panels (c, d)). At -920 mV vs Ag/AgCl two kinds of resonances are found, corresponding to CN⁻ adsorbed on Au- (CN⁻/Au) and Zn-sites (CN⁻/Zn).



Figure 8 - SFG spectra in the CN⁻ stretching region (black dotted lines) collected at: a) OCP (-830 mV vs Ag/AgCl), b) $V_{\text{bias}} = -1.25 \text{ V vs Ag/AgCl}$ with the respective fits (red lines).

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