

Supporting Information

Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM)[†]

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Christian Leppin,^a Astrid Peschel,^a Frederick Sebastian Meyer,^a Arne Langhoff,^a and Diethelm Johannsmann^{a*}

Resonance Curves as Determined with a Multi-Frequency Lockin Amplifier (MLA)

In the main text, it was stated that the multi-frequency lockin amplifier provides resonance curves with a few grid points only. Still, the resonance parameters can be derived from these sparsely populated experimental curves easily and robustly. Fig. S 1 shows examples.

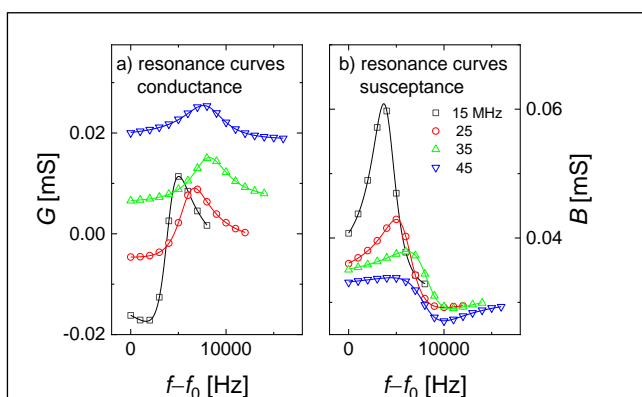


Fig. S 1

Real and imaginary part of the resonance curves. The spacing between the members of the comb was $\delta f_{\text{comb}} = 1$ kHz, resulting in a time resolution of 1 ms. The lines are fits with a phase-shifted Lorentzian. The phase-shifted Lorentzian is needed because of imperfect calibration.

Electrochemical Impedance Spectroscopy (EIS)

EIS was carried out in parallel to the QCM experiments. The spectra (Fig. S 2) were fitted with a Randles circuit expanded by a constant phase element:

$$Z \approx R_{\text{sol}} + \left(\frac{1}{R_{\text{CT}}} + i\omega^n Q_{\text{CPE}} \exp\left(i\frac{\pi}{2}(n-1)\right) \right)^{-1} \quad \text{Eq. 1}$$

$$\approx R_{\text{sol}} + \left(\frac{1}{R_{\text{CT}}} + i\omega C_{\text{DL}} \right)^{-1}$$

R_{sol} is the solution resistance, R_{CT} is the charge-transfer resistance, and C_{DL} is the double layer capacitance. The fits improved when the double layer capacitance, C_{DL} , was replaced with a constant-phase-element, CPE. The fits yielded $n \approx 0.85$, where $n = 1$ corresponds to a conventional double-layer capacitance. The RC-time was calculated as $R_{\text{sol}} Q_{\text{CPE}} \omega^{n-1}$, evaluated at $\omega = 2\pi \times 1$ kHz.

The charge transfer resistance, R_{CT} , was in the range of hundreds of kilo-ohms, while the solution resistance, R_{sol} , was hundreds of ohms. With R_{CT} replaced by infinity, the impedance, Z , can be approximated as

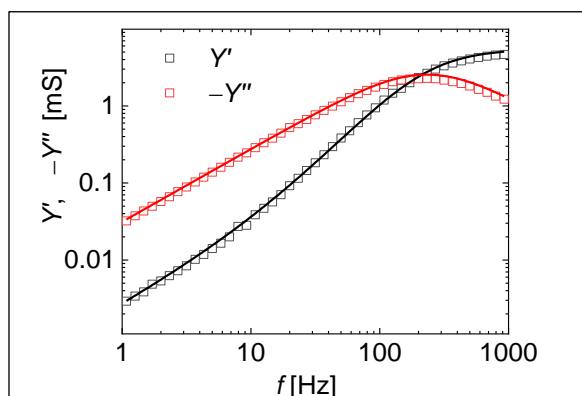


Fig. S 2

A typical EIS-spectrum in log-log form. The frequency, where Y' takes its maximum, is an inverse relaxation time, governed by the solution resistance, R_{sol} , and the double layer capacitance, C_{DL} . The sample was a 20 mM aqueous LiNO_3 solution.

^a Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany.

* Author for correspondence, electronic mail: johannsmann@pc.tu-clausthal.de

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$$Z \approx R_{\text{sol}} + \frac{1}{i\omega C_{\text{DL}}} = R_{\text{sol}} \left(1 + \frac{1}{i\omega\tau_{\text{RC}}} \right) \quad \text{Eq. 2}$$

The time $\tau_{\text{RC}} = R_{\text{sol}} Q_{\text{CPE}}\omega^{n-1}$ is of the same order of magnitude as the response time found with the voltage-modulation QCM. Charge reversal is mostly driven by a current from the bulk to the double layer (as opposed to a Faraday current).

Dependence of Amplitudes and Response Times on Concentration and Temperature

The concentration dependence of the amplitudes $\langle A/\Delta E \rangle$ in Fig. S 3 is nontrivial. Following Eq. 9 in the main text, the amplitude of the frequency response should be proportional to the charge response (blue stars in Fig. S 3). The charge increases with salt concentration (as expected), while the amplitudes in Δf decrease at high concentration.

Fig. S 4 shows the dependence of the inverse response times of the NH_4NO_3 electrolyte (20 mM) on inverse temperature. The response times show the same trend as the viscosity of water (blue stars, Refs. 1 and 2).

Calculation of the Density C-Coefficients

In the main text, changes in the viscosity-density product in the double layer were related to ion concentration, making use of the viscosity B-coefficients from the Jones-Dole equation³ and parameters called “density C-coefficients”, calculated from density increments of salts as tabulated in Ref. 4. An equation analogous to the Jones-Dole equation was formulated, which is

$$\frac{\rho(z)}{\rho_0} \approx 1 + \sum_i C_i c_i(z) \quad \text{Eq. 3}$$

This equation assumes additivity. The density shift of salt solutions is assumed to be the sum of contributions from the individual ions. The coefficients C_i were obtained by solving the matrix equation shown in Box 1. The routine `np.linalg.lstsq` from `numpy` was used. (A least-square algorithm is needed because the equation system is overdetermined.) Table 1 in the main text lists the density C-coefficients as derived this way. They are similar to the viscosity B-coefficients in magnitude.

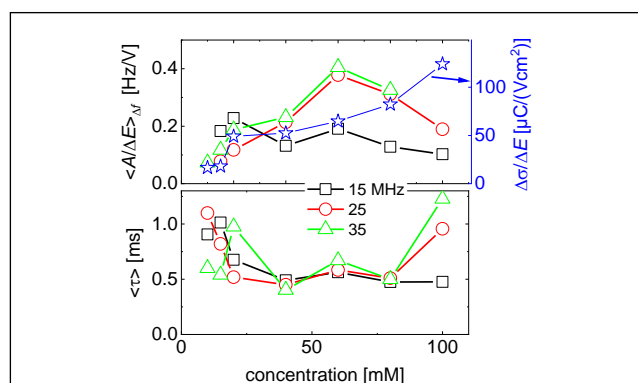


Fig. S 3

Dependence of amplitudes (from Δf) and response times on concentration for NH_4NO_3 . Blue stars (\star) show the charge in the double layer as inferred from EIS. Fractional error of the mean: $\langle A/\Delta E \rangle$: 2.9%; $\langle \tau \rangle$: 3.3%

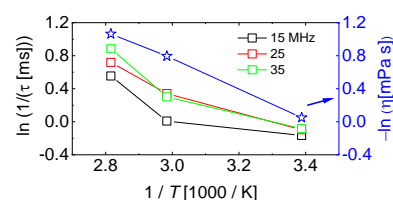


Fig. S 4

Dependence of the inverse response times on inverse temperature (NH_4NO_3). Blue stars (\star) show the viscosity of water following Refs. 1 and 2. Fractional error of the mean: $\ln(1/\tau)$: 3.2%

Li^+	Na^+	K^+	Cs^+	NH_4^+	F^-	Cl^-	Br^-	NO_3^-		
1	0	0	0	0	0	1	0	0	0.0245	LiCl
1	0	0	0	0	0	0	1	0	0.0603	LiBr
1	0	0	0	0	0	0	0	1	0.0441	LiNO ₃
0	1	0	0	0	1	0	0	0	0.0465	NaF
0	1	0	0	0	0	1	0	0	0.0449	NaCl
0	1	0	0	0	0	0	1	0	0.0836	NaBr
0	1	0	0	0	0	0	0	1	0.0630	NaNO ₃
0	0	1	0	0	1	0	0	0	0.0525	KF
0	0	1	0	0	0	1	0	0	0.0497	KCl
0	0	1	0	0	0	0	1	0	0.0906	KBr
0	0	1	0	0	0	0	0	1	0.0655	KNO ₃
0	0	0	1	0	1	0	0	0	0.1347	CsF
0	0	0	1	0	0	1	0	0	0.1327	CsCl
0	0	0	1	0	0	0	1	0	0.1693	CsBr
0	0	0	1	0	0	0	0	1	0.1503	CsNO ₃
0	0	0	0	1	1	0	0	0	0.0214	NH ₄ F
0	0	0	0	1	0	1	0	0	0.0206	NH ₄ Cl
0	0	0	0	1	0	0	1	0	0.0553	NH ₄ Br
0	0	0	0	1	0	0	0	1	0.0361	NH ₄ NO ₃

Box 1: Matrix used to calculate the density C-coefficients. The entries on the right-hand side (the density increments in units of L/mol of the salt solutions) were taken from Ref. 4.

Crystallographic Orientation of the Electrode Surface

In order to determine the fraction of Au(111) exposed to the electrolyte, XRD measurements were performed using an Empyrean diffractometer (Malvern Panalytical, Malvern, United Kingdom) in grazing incidence geometry with Cu-K α radiation (Fig. S 5). The angle between the sample plane and the incident beam was 0.3°. 2θ was scanned from 18° to 93° with a rate of 0.03° s $^{-1}$. The assignment of the peaks followed Ref. 5. The fraction of Au(111) was inferred from the sum of the peak integrals corresponding to Au(111) and (222), normalized to the sum of all peak integrals.⁶ A fraction of 75% Au(111) surface was obtained. The size of the crystallites was determined from the width of peaks and the Scherrer equation to be about 25 nm.

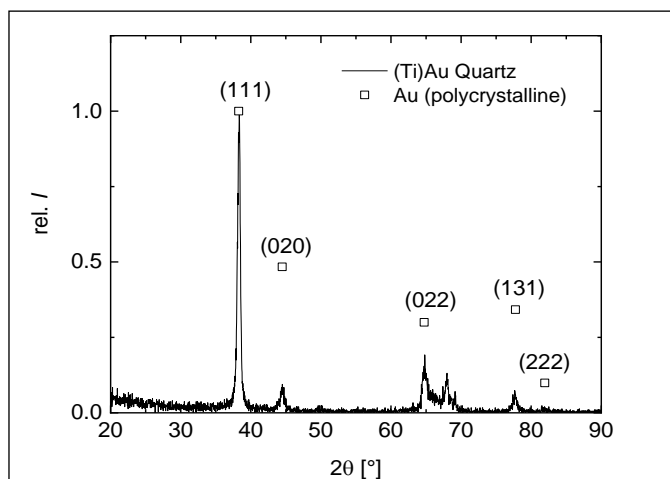


Fig. S 5

X-ray diffraction pattern from the electrode surface, showing that the electrode mostly exposes the Au(111) surface to the electrolyte. The intensities were normalized on the intensity of the Au(111) peak. Squares are the locations and the intensities of unoriented polycrystalline Au according Ref. 5.

Notes and References

- ¹ https://en.wikipedia.org/wiki/Temperature_dependence_of_viscosity, accessed on 15.07.2020
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