Electrochemical quartz crystal microbalance study on growth and property of the polymer deposit at gold electrodes during oxidation of dopamine in aqueous solutions

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Abstract

Polymer growth at Au electrodes during cyclic voltammetric oxidation of dopamine (DA) in aqueous solutions was investigated as functions of DA concentration, solution pH and potential-sweep rate with the use of electrochemical quartz crystal microbalance technique. When the DA concentration was \(2 \times 10^{-4}\) M or above and the solution pH was 3.86 or above, the intramolecular cyclization of the first-step oxidation product of DA occurred significantly and further isomerization and oxidation of the cyclization product led to polymer growth at an Au electrode. An ECECEE mechanism for DA oxidation and subsequent polymerization of the oxidation product (5,6-indolequinone) at favorable pH is suggested. The poly(indole)-like polymerization pathway was acceptably supported by comparative minigrid-electrode experiments via Fourier transform infrared characterization of poly(indole) and the polymer from DA oxidation. The quasi first-order rate constant of the intramolecular cyclization was estimated at several pH values by cyclic voltammetry. It was also found that the intramolecular cyclization and subsequent polymer deposition at the electrode can be notably inhibited by using various high-concentration supporting electrolytes, with inhibition sequences as \(\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{gluconate} > \text{F}^- > \text{citrate} > \text{CH}_3\text{COO}^-\) for anions and \(\text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Cs}^+ > \text{Rb}^+\) for cations. In addition, an Au electrode modified with the polymer from DA oxidation exhibited attractive cationic permselectivity, namely, effectively blocking the electrochemical reactions of anionic ferrocyanide and ascorbic acid (AA) while well retaining the electrochemical activities of hexaammineruthenium (III) and DA as cationic species. A 500-Hz polymer film could effectively block the redox current of AA up to 2.0 mM. The semi-derivative voltammetric peak height for DA oxidation was linear with DA concentration up to 1.3 \(\times 10^{-7}\) M, with sensitivities of 0.0766 and 0.119 \(\text{A} \text{s}^{1/2}/\text{M}\), as well as lower detection limits of 4 \(\times 10^{-7}\) and 2 \(\times 10^{-7}\) M \((S/N = 3)\) in a phosphate buffer solution without AA and with 1.0 mM coexisting AA, respectively.

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1. Introduction

Dopamine (DA) is an important neurotransmitter. Extreme abnormalities of DA concentration levels may lead to several diseases, e.g., Parkinson’s disease. Many researchers have thus been attracted to work on the research and determination of DA. DA can be investigated and determined by electrochemical methods due to its intrinsic redox nature \([1,2]\). However, polymerization of the oxidation product of DA leads to polymer deposition at the electrode and thus a gradual loss of the electrode activity (electrode poisoning or fouling) \([3–5]\), though the growth and properties of this polymer is not so clearly clarified in literatures. Moreover, ascorbic acid (AA) acts as a common interfering substance in DA electroanalysis, because it is usually of higher concentrations in biological samples but is not oxidized at a potential close to that for DA. Therefore, DA electroanalysis is generally conducted at an electrode modified with a film that is permselective to DA molecules \([6,7]\).
The electrochemical quartz crystal microbalance (EQCM), which uses a piezoelectric quartz crystal (PQC) as its central sensing element, has been well established as a powerful tool capable of tracing an electrode-mass change down to the nanogram level (usually equivalent to sub-monolayer surface modification) in electrochemical processes, and thus it has been widely used in studying various thin solid films [8]. There are mainly two protocols for EQCM construction. A conventional oscillation-circuit/frequency-counter routine was first employed for EQCM construction due mainly to its simplicity and cost effectiveness [8], however, generally the piezoelectric information only on the oscillating frequency can be acquired. Later, the more sophisticated impedance-/network-analysis method has also been proposed for EQCM construction, which yields multidimensional piezoelectric information and thus characterizes the PQC resonance more completely, generally via impedance analysis of a Butterworth–van Dyke (BVD) equivalent electrical circuit [8–16]. The BVD circuit consists of a motional arm in parallel with a static capacitance ($C_0$) and thus is valid for mass estimation [8–16], however, generally the piezoelectric information and thus characterizes the PQC resonance more completely, generally via impedance analysis of a Butterworth–van Dyke (BVD) equivalent electrical circuit [8–16]. The BVD circuit consists of a motional arm in parallel with a static capacitance ($C_0$). The motional arm contains three equivalent circuit elements in series, i.e., the motional resistance ($R_1$), the motional inductance ($L_1$) and the motional capacitance ($C_1$) [8–16]. Therefore, the impedance-analysis-based EQCM is advantageous for its providing multiple piezoelectric information, including the resonant frequency ($f_0 = 1/(2\pi \sqrt{L_1 C_1})$) and various equivalent circuit parameters, which is especially helpful to discern and/or distinguish simultaneous mass and viscos density effects in a practical system, as quantitatively explained by the following equations.

The net mass effect on the frequency response can be well expressed by the Sauerbrey equation, which correlates the change of electrode mass ($\Delta m$ in g) resulted from deposition and dissolution of a rigid, thin and uniformly distributed film with the shift of EQCM resonant frequency ($\Delta f_0$ in Hz) [17].

$$\Delta f_0 = -2.264 \times 10^{-6} f_0^2 \Delta m / A,$$

where $f_0$ is the fundamental frequency of the unperturbed crystal in Hz, and $A$ is the piezoelectrically active electrode area in cm$^2$.

As for the net viscos density effect resulting for loading and removal of a Newtonian liquid, the following relationship holds:

$$\Delta R_{1L} = -4\pi L_{1q} \Delta f_{0L} \sqrt{f_0^4 / f_{0q} C_{66}} \approx -4\pi L_{1q} \Delta f_{0L},$$

where $\Delta f_{0L}$ in Hz and $\Delta R_{1L}$ in $\Omega$ are changes in $f_0$ and $R_1$ due to pure variations of the solution density and viscosity, respectively, $\mu_q (2.947 \times 10^{10}$ N m$^{-2}$) is the shear modulus for the AT-cut quartz, $L_{1q}$ in H is the motional inductance for the PQC in air, and $C_{66}$ ($2.957 \times 10^{10}$ N m$^{-2}$) is the lossy piezoelectrically stiffened quartz elastic constant [9,11–16].

According to Eq. (2), the characteristic slope value of $\Delta f_{0L} / \Delta R_{1L}$ for a net density/viscosity effect on the resonance of 9 MHz PQC is $\sim -10$ Hz $^{-1}$. Therefore, if the absolute value of $\Delta f_0 / \Delta R_1$ in a practical process is significantly larger than the characteristic value of $\Delta f_{0L} / \Delta R_{1L}$ for a net viscosity effect, the mass effect should govern the frequency response in this process and the Sauerbrrey equation is valid for mass estimation, since a net mass effect changes the frequency as given in Eq. (1), but the simultaneous change in $R_1$ is negligible. Otherwise, the simultaneous viscos density effect should be carefully considered in mass estimation.

In this work, polymer growth during oxidation of DA at Au electrodes is investigated via the EQCM method for the first time, and effects of solution pH, DA concentration, and potential sweep rate are examined. The anti-polymerization effects of various supporting electrolytes at high concentrations are discovered and investigated in detail. The polymer film is found to be permselective toward cations, allowing its potential use as a permselective film for DA electroanalysis in the presence of ascorbic acid.

### 2. Experimental details

The EQCM setup used in this work is described in Fig. 1, which allowed simultaneous measurements of PQC electro-acoustic admittance via an HP4395A impedance analyzer and electrochemical signals via a CHI600A electrochemical workstation (CH Instruments, USA). Admittance measurements were conducted under conditions of 101 points, a frequency span of 40 kHz covering PQC’s resonant frequency, IF BW of 10 kHz and source power of 0.5 dBm. Synchronous conductance ($G$) and susceptance ($B$) measurements were conducted on the HP4395A controlled by a user-written Visual Basic (VB) 5.0 program. Equivalent circuit parameters were obtained at a time interval of ca. 1 s under control of the same VB program, via simultaneous nonlinear fitting of experimental $G$ and $B$ data to the BVD circuit.

AT-cut 9 MHz piezoelectric quartz crystals (1.25 cm in diameter) were used here. An Au electrode of 0.6-cm diameter on one side of the PQC was in contact with the solution and served as the working electrode (WE), while a gold electrode on the other side of the PQC was located in air. The gold electrode (WE) surface was treated with $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ (v/v 3 : 1) for 5 s.
and then thoroughly rinsed with pure water prior to use. A saturated KCl calomel electrode (SCE) served as the reference electrode (RE), and all potentials in this work were referenced to it. A platinum plate served as the counter electrode (CE).

Fourier transform infrared (FTIR) spectra were collected on a Nicolet Nexus 670 FTIR instrument in the transmission mode. Experimental operations are depicted as follows. Two pieces of transparent minigrid electrodes of stainless steel in 1.8 × 2.4 cm size were cut, followed by coating the minigrid electrodes with thin-layer gold through sputtering from a gold target of 99.99% purity for 40 min under conditions of 7 mm Hg air atmosphere and 2 mA current (Zhongkekeyi SBC-12 ion coater, Beijing). The details of minigrid specification are as follows, diameter of metal wire = 25 μm, size of metal wires-enclosed rectangular hole = 30 × 30 μm, and both holes and wires are uniformly distributed, as examined by an optical microscope (Olympus CH30, Japan). The prepared Au minigrid electrodes were used as the WE during polymerization, which was partially immersed in a phosphate buffer solution (PBS) containing 50 mM DA or 5 mM indole. After cyclic voltammetric polymerization for 2 h (20 mV/s, potential cycling between 0 and 1.0 V), the polymer-modified Au minigrid electrodes were dried and then subject to FTIR measurements in the transmission mode. All FTIR spectra were collected at an average factor of 100 and a wavenumber resolution of 4 cm⁻¹. The parts of bare Au minigrid electrodes that were not immersed in the polymerization bath were used as the reference.

DA (Fluka 56610) was used as received. All other reagents were of analytical grade or better quality. The PBS contained 0.3 M NaClO₄ and 0.1 M NaH₂PO₄–Na₂HPO₄ (pH = 7.4). The initial Britton–Rubinson (B–R) buffer solution (pH = 1.91) contained 0.2 M Na₂SO₄ + 0.04 M mixed acids (phosphoric acid + acetic acid + boric acid). The solution pH was measured via a pH meter (Xiaoshan Analytical Instruments Factory, China). All solutions were prepared with twice distilled water. All experiments were conducted at room temperature (20 ± 2 °C).

3. Results and discussion

3.1. Preliminary description for EQCM monitoring of DA oxidation and related polymer growth

The electrochemical pathway for DA has been proposed to occur via an ECE mechanism, as given by the first 3 reactions/steps in Scheme 1 [18–20], namely, DA is oxidized to dopaminequinone (DAQ); the intramolecular cyclization of DAQ via 1,4-Michael addition leads to the more readily oxidizable leucodopaminechrome (LDAC); and then LDAC is oxidized to dopaminechrome (DAC). DAC can further undergo polymerization reactions on the electrode surface, yielding deposited melanin-like polymer responsible for the gradual loss of electrode activity. In Scheme 1, the “E” denotes the electrochemical reactions while the “C” denotes the chemical reactions.

Fig. 2 shows responses of current, ΔIₒ, and ΔRᵢ to 20-cycle potential sweeps between −0.5 and 0.5 V in the PBS (pH = 7.4) containing 2.0 mM DA. As is seen, an oxidation peak at ca.

![Scheme 1](image-url)

Scheme 1. The ECE mechanism for DA electrochemistry [18–20] and the pathway for polymer growth suggested in this work (starts from DAC). The site numbering of 5,6-indolequinone is used as reference in the text.
0.19 V ($P_{a1}$) was observed in the first positive scan, which is attributed to the oxidation of DA, while two current peaks were observed in the subsequent reversal scan, which may be attributed to reduction of DAQ ($P_{c1}$, at ca. 0.09 V) and DAC as the intramolecular cyclization reaction product of DAQ ($P_{c2}$, at ca. −0.31 V), as given in Scheme 1. A new oxidation peak at ca. −0.25 V ($P_{a2}$) was obtained in the second positive scan, which may be attributed to the oxidation of LDAC. Notable decreases in $f_0$ were observed cycle by cycle during DA oxidation (near $P_{a1}$), with very small increases in $R_1$ ($\Delta f_0/\Delta R_1 \approx -150$ Hz $\Omega^{-1}$), and the simultaneous responses of the half-peak width of the conductance curve and the static capacitance were also very small (not shown) [15], demonstrating that a rigid film was growing at the Au electrode during DA oxidation. Simultaneously, the heights of all current peaks were decreased cycle by cycle. Therefore, the film deposited was insulating in this PBS medium, since no current peaks associated with the redox processes of the polymer itself were observed, instead, peak heights of $P_{a1}$ and $P_{c1}$ were decreased and the peak-to-peak separation of $P_{a1}/P_{c1}$ and $P_{a2}/P_{c2}$ was increased cycle by cycle during potential cycling, indicating a gradual decrease in the electrode activity toward DA oxidation due to deposition of a polymer layer as an electron-transfer barrier. Experimentally, we found that the polymer film deposited was attached to the EQCM electrode surface very strongly, and the frequency change was within ±5 Hz during 100-cycle potential sweeps between −0.1 and 0.5 V in PBS (pH=7.4). However, the film could be easily removed by rinsing with H$_2$SO$_4$+H$_2$O$_2$ (v/v 3:1), which is favorable for recycled use of the EQCM electrode.

### 3.2. The effect of pH

The effect of solution pH on the polymerization was examined, as shown in Fig. 3. At pH 1.91 and 3.86, the $P_{a2}/P_{c2}$ redox peaks were very difficult to be identified from their current baselines, even at pH 5.04 they were not so clearly visible. However, at pH 7.02, 9.11 and 11.08, they became very obvious. This finding suggests that the presence of protons of relatively high concentration inhibited the coupled intramolecular cyclization of DAQ. Redox peaks of $P_{a1}$, $P_{c1}$, $P_{a2}$, and $P_{c2}$ were also shifted negatively with the increase of solution pH, and the relationships between the peak potential and solution pH satisfy the following equations, namely, $E_{P_{a1}} = -0.051 \pm 0.571$ (r=0.9984) for $P_{a1}$ (from pH 1.91 to 11.08), $E_{P_{c1}} = -0.050 \pm 0.494$ (r=0.9935) for $P_{c1}$ (from pH 1.91 to 11.08), $E_{P_{a2}} = -0.057 \pm 0.138$ (r=0.9997) for $P_{a2}$ (from pH 5.04 to 11.08), and $E_{P_{c2}} = -0.050 \pm 0.176$ (r=0.9950) for $P_{c2}$ (from pH 5.04 to 11.08), respectively. The nearly Nernstian slopes obtained here suggest one-proton-per-electron processes for all the four peaks. The full pathway...
suggested in this work for DA oxidation virtually involves an ECECEE mechanism, as shown in Scheme 1, however, the redox peaks for the 5,6-indolequinone/5,6-dihidroxylindole couple (the third “E” step) and the oxidation current of polymer deposition (the last “E” step) are seemingly absent in the cyclic voltammograms shown. A plausible explanation for this phenomenon is that the peak potentials of the third “E” step may be very close to those of the DAC/LDAC couple (the second “E” step), and the oxidation currents during polymerization in the last “E” step may be buried in the currents for DA oxidation (note the peak-tailing shape for DA-oxidation currents). We may thus regard the full pathway of DA oxidation as a series of processes involving transfer of \((6 + x)\) protons and \((6 + x)\) electrons in total, where \(x\) is the number of protons or electrons transferred in the last “E” step, and thus the nearly Nernstian slopes for peak potentials of \(P_{a1}\), \(P_{c1}\), \(P_{a2}\) and \(P_{c2}\) are expected. Simultaneously, the frequency-decrease amplitude after 20-cycle potential sweeps was positively correlated with the solution pH, as shown in Fig. 3 (left), and at 1.91 no any frequency decrease was observed, suggesting the polymer growth occurred only when the solution pH was ca. pH 4 or above. An overall consideration on the experimental findings given in Fig. 3 leads to a believable conclusion that the precondition for polymer growth is the occurrence of the intramolecular cyclization of DA, whose product can evolve to a polymer deposit during potential cycling.

3.3. The effect of DA concentration

The effect of DA concentration on the polymerization was studied in a PBS buffer (pH = 7.4), and the results are given in Fig. 4. As is seen, the frequency-decrease amplitude after 20-cycle cyclic voltammetric oxidation of DA was positively correlated with concentration of DA, and at a DA concentration of \(2 \times 10^{-5} \) M the frequency decrease was barely observable.
but above $2 \times 10^{-4}$ M it became obvious. This finding is not strange, since, at a very low DA concentration, the concentration of the DA-oxidation product as the monomer was too small to appear as a polymer deposit on the Au electrode surface. It is worth pointing out that the cathodic current peak at $\sim -0.35$ V, which is more visible in a very dilute DA solution, is assigned to irreversible reduction of the soluble oxygen present in the solution, as supported by a blank experiment using a bare Au electrode in the absence of DA, rather than the reversible reduction of DAC or 5,6-indolequinone (Scheme 1), since no equivalent anodic companions were found here. With the decrease of DA concentration, current peak of $P_{c2}$ became less visible, thus highlighting the currents for irreversible reduction of soluble oxygen at negative potentials. In addition, at a very small DA concentration the polymer deposition became less significant, and thus the electrode surface may be somewhat activated toward oxygen reduction.

### 3.4. The effect of potential sweep rate

Also, the cyclic voltammograms were recorded at various potential sweep rates to examine the kinetics for the coupled intramolecular cyclization reaction, as shown in Fig. 5. Current peaks of $P_{a2}$ and $P_{c2}$ became more and more unclear with the increase of potential scan rate, and experimentally at scan rates above ca. 1 V/s, they became almost invisible. This finding demonstrates that the coupled intramolecular cyclization of 0.7-s reaction time (1 V/s, from the half-peak potential for DA oxidation to the half-peak potential of subsequent reduction of DAQ) did not produce reaction product sufficient for electrochemical detection. Peak currents of $P_{a1}$ ($P_{c1}$) were linear with the square root of scan rate from 10 (50) to 1000 mV/s, demonstrating that $P_{a1}$ was a diffusion-controlled process but $P_{c1}$ was additionally affected by depletion of DAQ via the coupled intramolecular cyclization. However, $P_{a2}$ and $P_{c2}$ versus scan rate displayed peak-type responses, because two opposite factors took effect here, namely, a slower potential sweep rate led to a lengthened period for intramolecular cyclization and thus to heightened $P_{a2}$ and $P_{c2}$, but at a slower sweep rate, the diffusion currents were intrinsically decreased. The coupled intramolecular cyclization may be treated as a quasi first-order reaction with a rate constant of $k_1$. Since the ECE mechanism shown in Scheme 1 via the first 3 steps is complicated by polymer growth that decreases the electrode activity, only a rough estimation of $k_1$ is given here on the basis of the absolute value of ratio of $i_{P_{c1}}$ to $i_{P_{a1}}$. Since $|i_{P_{c1}}/i_{P_{a1}}|=0.5$ at $\sim 50$ mV/s, the half life of the reactant of intramolecular cyclization, $t_{1/2}$, should be equivalent to the reaction-time length of ca. 14 s when the coupled intramolecular cyclization took place, which is estimated from the moment when the reactant of intramolecular cyclization was generated ($\sim 0.14$ V) to the moment when the intramolecular cyclization was stopped at $\sim 0.16$ V during reversal cathodic sweep. Therefore, $k_1$ can be roughly estimated to be $k_1=\ln 2/t_{1/2}=0.05$ s$^{-1}$ in this medium. Similarly, we obtain $k_1$ values of 0.0029, 0.02 and 0.08 s$^{-1}$ at pH 5.0, 6.7, and 9.1, respectively, indicating the elevated facility of the coupled intramolecular cyclization at a higher pH value.

### 3.5. The concentration effects of various supporting electrolytes

In this work, the concentration effects of various supporting electrolytes on the polymerization during DA oxidation were discovered and examined. As is seen from Fig. 6, with the increase of KNO$_3$ concentration from 0.10 to 0.50, 1.0 and finally to 2.0 M, the frequency response decreased notably, suggesting that the polymer growth is more and more inhibited with the increase of KNO$_3$ concentration. It is well known that, for an EC or ECE mechanism, the peak–current ratio of $P_{c1}$ to $P_{a1}$ can be taken as a measure for less or more extent in evolvement of the coupled chemical reaction [21], here the intramolecular cyclization of DAQ. In addition, the ratio of $|i_{P_{c1}}/i_{P_{a1}}|$ increased with the increase of KNO$_3$ concentration, demonstrating further that the intramolecular cyclization of DA stands as a premise for the polymer growth. The $k_1$ values for 0.1, 0.5, 1.0 and 2.0 M KNO$_3$ are estimated by the above method to be 0.045, 0.025, 0.015, and 0.012 s$^{-1}$, respectively, also demonstrating that the intramolecular cyclization of DA can be somewhat inhibited at a higher KNO$_3$ concentration.
Furthermore, the effects of different ions on the polymer growth were examined via the $|P_{c1}/P_{a1}|$ criterion, as shown in Fig. 7, where 0.5 M Na$^+$ and 0.5 M NO$_3^-$ were used for comparative examinations of various anions and cations, respectively. It was found that the polymerization–inhibition sequences follows ClO$_4^-$ > NO$_3^-$ > SO$_4^{2-}$ > gluconate > F$^-$ > citrate > CH$_3$COO$^-$ for anions and NH$_4^+$ > Na$^+$ > Li$^+$ > K$^+$ > Cs$^+$ > Rb$^+$ for cations, respectively. This finding should imply that different supporting electrolytes must affect the nucleophilic ability of nitrogen atoms in DAQ, the facility of the intramolecular cyclization and subsequent polymerization growth, and thus the DA system may act as a good system to study the electrolyte effects on related organic reactions/synthesis via electrochemical methods, though the exact mechanism behind the present finding requires a much more detailed study. Moreover, this finding may be of potential use in reducing the electrode-fouling phenomenon commonly encountered in DA electrochemistry [3–5], just simply by increasing the concentration of supporting electrolyte, rather than by introducing foreign additives.

3.6. Discussion on polymerization mechanism

Although the ECE mechanism for DA, as given in Scheme 1 via the first 3 steps, is well known, however, the mechanism for polymer growth during DA electro-oxidation has been rarely discussed in literatures. Considering that the formation of DAC is definitely necessary for the polymer growth, as aforementioned, we thus believe that the polymerization reaction should start from DAC as the initial reactant. However, it is most unlikely that DAC can be considered as a direct monomer to start common phenol-like and/or aniline-like polymerization, as the para-positions of either oxygen or nitrogen atoms are occupied in DAC, thus we speculate that part DAC molecules may evolve to the more stable 5,6-dihydroindole molecules of two aromatic rings via isomerization, and then 5,6-indolequinone is electropolymerized via a poly(indole)-like pathway [22], as also given in Scheme 1. If this is the case, the electrochemical behavior of the polymer from DA oxidation is expected to be similar to poly(indole). As shown in Fig. 8, two couples of redox peaks of the polymer were found in 1.0 M aqueous HClO$_4$ at high potentials, being similar to poly(indole) [22], and the peak current at ca. 0.6 V varied linearly with the scan rate between 20 to 200 mV/s, as predicted theoretically for thin-layer behavior of surface-confined electroactive species. However, the large cathodic current peak observed at $-0.1$ V can be assigned to the irreversible reduction of soluble oxygen in this acidic solution, as supported by a blank experiment using a bare Au electrode. In addition, the peak height at ca. $-0.1$ V is found to be linear with the square root of scan rate, indicating that this process resulted from diffusion-controlled reduction of solution species, rather than thin-layer behavior of surface-confined electroactive species.

Fig. 9 shows the FTIR spectra of poly(indole) and polymer from DA oxidation for comparison, which are very similar in shape. The major FTIR bands are briefly discussed as follows.
[23–25]. (1) Both spectra do not present significant bands to N–H bonds in their stretching (≈3400 cm$^{-1}$) vibration or other modes, demonstrating that the polymerization is most likely via 1-position coupling in the pyrrole ring [23]; (2) Bands from 1650 to 1450 cm$^{-1}$ are attributed to stretching of aromatic C–C bonds characteristic of indoles [24]; (3) Bands from 950 to 650 cm$^{-1}$ are attributed to out-of-plane deformation of aromatic C–H bonds [25]; (4) No significant bands in the spectrum of polymer from DA oxidation could be assigned to stretching or deformation vibrations of O–H and C=O bonds. However, a broad band recorded at 1260 cm$^{-1}$ may be ascribed to out-of-plane deformation of C–O–C with π–π conjugation (here O atoms bond with aromatic rings) [25], which supports well the fact that the quinone/hydroquinone redox switching was not significant in 1.0 M aqueous HClO$_4$ (Fig. 8). Therefore, we may conclude that the polymer from DA electrooxidation can be most likely speculated as poly(5,6-indolequinone), and many oxygen atoms therein may have developed C–O–C chains during the poly(indole)-like electro-polymerization [26,27].

Fig. 10. Cyclic voltammograms of 2.0 mM DA (a), 2.0 mM Ru(NH$_3$)$_3$Cl$_3$ (b), 2.0 mM K$_4$Fe(CN)$_6$ (c) and AA at several concentrations (d) in PBS buffers (pH= 7.4) at bare (solid lines) and 500-Hz-polymer-modified Au electrodes (dashed lines). $v=20$ mV/s. Concentrations of AA for curves 1–5 are 1.0, 2.0, 5.0, 7.0, and 10 mM, and that for the bare Au electrode is 2.0 mM.

Fig. 11. Cyclic voltammograms and related first-order semi-derivatives ($i_{sd}$) for a 500-Hz-film-modified Au electrode in AA-free PBS buffer (pH= 7.4) containing DA of different concentrations (left) as well as the semi-derivative peak current ($i_{p-sd}$) versus DA concentration in PBS solutions containing 0 (a), 0.50 (b) or 1.0 (c) mM AA (right). DA concentrations for curves 1–9 (left) are 0.400, 0.800, 1.20, 3.20, 8.17, 13.1, 51.8, 98.1 and 184 mM, respectively.
3.7. Cationic permeselectivity of the polymer-modified electrodes

Fig. 10 shows the cyclic voltammograms for 2.0 mM DA, 2.0 mM Ru(NH₃)₆³⁺, and 2.0 mM Fe(CN)₆⁴⁻ and AA at several concentrations in PBS buffer (pH 7.4) at Au electrodes modified with 500-Hz polymer from DA electrooxidation, with a bare Au electrode as a comparison. As is seen, the 500-Hz film effectively blocked the electrochemical reactions of anionic species, 2 mM ferrocyanide and AA up to 2 mM, while well retaining the electrochemical activities of hexaaaminemer-uthenium (III) and DA as cationic species, implying that the polymer layer was permeable to cationic species. Experimentally, a thicker film provided better repellent ability toward AA but simultaneously inhibited DA oxidation to a greater degree, and a thinner film gave worse AA-repellent ability. Accordingly, modification of 500-Hz polymer is selected for the following experiments.

Cyclic voltammograms of DA recorded at an Au electrode modified with a polymer film from dopamine electrooxidation and relevant first-order semi-derivatives are shown in Fig. 11. The semi-derivative treatments of cyclic voltammograms, by using the data-analysis function embedded in CHI660A software, are given here for obtaining peaks with better resolution. The semi-derivative peak response was linear with the DA concentration up to 13 µM, and the detection limits for DA (S/N = 3) were 0.4 µM without AA, and 0.2 µM with 1.0 mM AA coexisting in the measuring solution, respectively. The response sensitivity values (slopes) were 0.0766 µA s⁻¹/µM without AA and 0.119 µA s⁻¹/µM with 1.0 mM AA, respectively. The finding that the presence of AA increased the DA-oxidation current agrees with those reported previously [28,29], due probably to the chemical regeneration of DA through an AA-catalyzed reduction of the electrooxidation product of DA (EC⁺ mechanism). The sensitivity and lower detection limit for DA reported here may have fitted DA detection in DA pharmaceuticals [30].

4. Conclusion

In summary, the EQCM technique has revealed that, when the DA concentration was ca. 2 × 10⁻⁴ M or above and the solution pH was 3.86 or above, the coupled intramolecular cyclization of DAQ occurred significantly and the further oxidation of DAQ led to polymer growth at the Au electrode. A relevant ECCECEE mechanism has been suggested and discussed, where the poly(indole)-like polymerization pathway has also been acceptably supported by comparative minigrid-electrode experiments via FTIR characterization of poly(indole) film and the polymer film from DA electrooxidation. The quasi first-order rate constants of the coupled intramolecular cyclization were estimated through examining the effects of potential sweep rate. It has been discovered that the coupled intramolecular cyclization reaction and polymer growth can be significantly inhibited when using various higher-concentration supporting electrolytes. This polymer was found to exhibit attractive cationic permeselectivity and thus may be used as a good candidate for permeselective electroanalysis of DA. In addition, we have found that the polymer from DA oxidation is a good matrix for immobilization of enzyme and other biomaterials, related results will be reported in separate papers.

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