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Nickel Thin Film Resonantly Generated at a Rate of Megahertz

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Resonant frequencies at which masses of Ni thin films deposited from a nickel sulfamate solution significantly increase are observed using a rectangular pulse current technique having a frequency of the megahertz scale. The resonant frequency spacing between the neighboring resonant frequencies keeps a constant value of 0.2 MHz. The presence of many resonant frequencies and the constant resonant frequency spacing show an energy level transition between an electron at the Fermi energy level in an electrode and a nickel sulfamate ion characterized by a quantized rotational energy level. In addition, at a frequency beyond the highest resonant frequency the normalized deposition mass that keeps a constant value nearly equal to 1 is found. The frequency named as a non-capacitative frequency shifts to a lower frequency with an increase in the solution temperature. This indicates that the electric double layer in the solution loses a capacitative property owing to nickel sulfamate ions that do not rotate at the applied pulse frequency.

Keywords: resonant frequency; electrodeposition; energy level transition; Ni thin film; quantized rotational energy level

1. INTRODUCTION

Synthesis of Ni films is often carried out by electrodeposition. The electron transfer occurring during Ni electrodeposition, $Ni^{+2}+2e^{-}\rightarrow Ni$, which is referred to as an energy level transition [1] that describes the transfer of an electron in an electrode (or Ni film) to a Ni^{+2} in a solution, takes place in an electric double layer formed between an electrode and a solution. As is well known in direct current and low frequency current electrodeposition [2-6], electrodeposition occurs among many electrochemical reaction paths, along which the Ni ion changes to the Ni atom. Hence, there have been very few studies in which electrodeposition has been performed at a high frequency of the megahertz scale.

When electrodeposition is performed by a current having a frequency of the megahertz scale, a large change in the deposited mass generated resonantly at the frequency of this current may be observed. This is because the electron transfer having a reaction time much shorter than a few microseconds is expected to be chosen from among the many possible electrochemical paths. The mass measurement of the Ni film formed in high frequency electrodeposition provides simple and evident proof for the resonantly generated Ni electrodeposition at around the resonant frequency.

We have reported [7] the deposit mass of nickel dependent on frequency well described by an electric circuit model equivalent to the electric double layer. The deposit mass is shown to decrease with the frequency and approach a constant value, however, no resonant behavior in the electrodeposit mass has been found at a frequency less than 10 kHz.

In general, the energy level transition is of many different types owing to the energy difference between the states [8]. The Ni^{+2} ion that is included in a complex salt has 8 degenerate electrons filling the 3d orbital, in which the energy level is split by the crystal field, vibrations, and rotations [9]. The effect of an electric field on the vibrational and rotational motion of a linear molecule has been investigated [10-11]. Whereas the electron at the Fermi-level in the electrode transfers to a ground state of the Ni ion in the solution, no experimental studies related to a selection rule or the transition frequency that demonstrates that momentum is conserved have been reported, to the best of our knowledge. This suggests that the Fermi energy level of the electron in the electrode lies closely to the energy level of the Ni ion excited by the transition; that is, the energy difference will be less than the energy of the microwave frequency used for rotational-vibrational spectroscopy [12].

A goal of this work is to show that the resonant frequencies at which the masses of the Ni film significantly change are observed in the frequency range of 0.1 to 2.5 MHz during electrodeposition.

2. EXPERIMENTAL SET UP

A nickel specimen of size 30x10 mm^2 and nickel plate of 50x40 mm^2 were prepared to serve as a cathode and anode electrode. One side of the nickel specimen was coated with an insulating thin film to prevent electrodeposition. The two electrodes, cleaned by a wet process, were placed parallel to each other in an electrochemical cell filled with an aqueous solution including the following components ($mol\ L^{-1}$): nickel sulfamate, 1.86; and boric acid, 0.647. The solution was strained using a membrane with a pore size of 0.17 μm. The solution was maintained at temperatures of 298, 308, and 318 K.

In this study, nickel electrodeposition from a nickel sulfamate solution was chosen because of a high current efficiency almost equal to 100 % in direct current electrodeposition [7]. The nickel specimen was immersed to 10 mm in depth in the electrolyte solution. Hence, the area of the anode electrode was about 40 times as large as that of the cathode electrode. Thus, we can ignore the impedance in series of the anode electrode in the solution in comparison with those of the cathode electrode.

A function generator was used to supply the rectangular pulse voltage. A metal film resistor (KOA Corporation) of 51 Ω, whose impedance remained constant at frequencies below 80 MHz, was connected in series with an electrochemical cell comprising an anode, a cathode, and the solution mentioned above. The rectangular current pulse flowing in the electrochemical cell was calculated from a voltage drop across the metal film resistor measured with a digital storage oscilloscope. The on-time of the current was chosen to be equal to the off-time of the current. Figure 1 shows the rectangular current pulse having an average peak current amplitude of 22.3 mA/cm^2 and a frequency of 1 MHz at a solution temperature of 298 K, from which a deposition time for the deposited mass of 5 mg was determined for a current efficiency of 100 %.

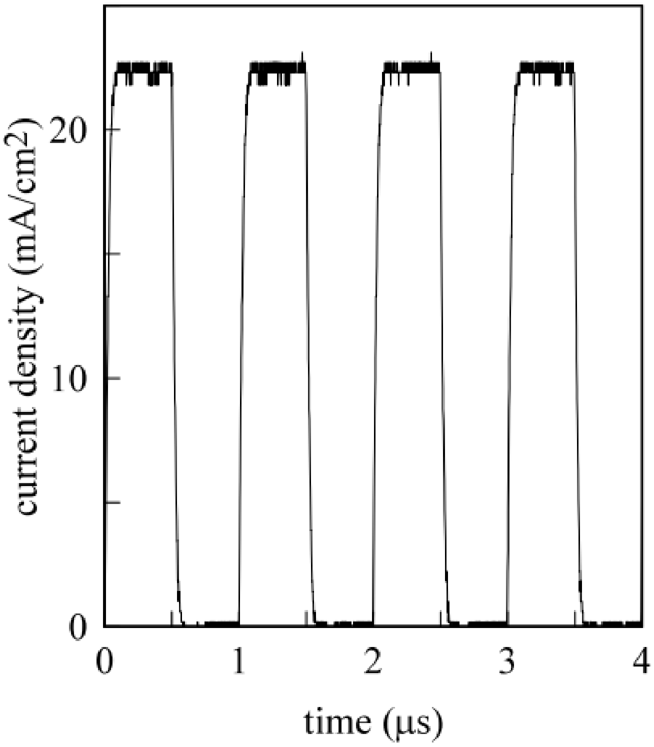

Figure 1. Typical rectangular current pulse having an amplitude of 22.3 mA/cm^2 and a frequency of 1.0 MHz. The rectangular current pulse was determined by the voltage drop across the resistor measured with the digital storage oscilloscope.

The rectangular current pulse flowed in the electrochemical cell during the calculated deposition time. After deposition, the actual Ni films electrodeposited on the nickel electrode were weighed to the precision of 0.1 mg with an electric balance (AND HR-60). The ideal Ni electrodeposited mass of 5 mg for a current efficiency of 100 % was used as the ideal deposited mass when the deposited mass was normalized.

3. RESULTS AND DISCUSSION

Figure 2 shows the normalized mass of the Ni film electrodeposited at a solution temperature of 298K over a frequency range from 10 Hz to 2.5 MHz. The normalized deposit mass at a frequency less than 0.3MHz has a constant value of 0.81 except for the frequency nearly equal to 0 Hz. So as to see the deposit mass at a frequency lower than an order of magnitude of kHz in detail, Figure 3 shows the normalized deposit mass at a frequency of 10 Hz to 2 kHz. As the low frequency-dependence of the Ni electrodeposited mass has been reported in detail elsewhere [7, 13], here, the result is only briefly explained.

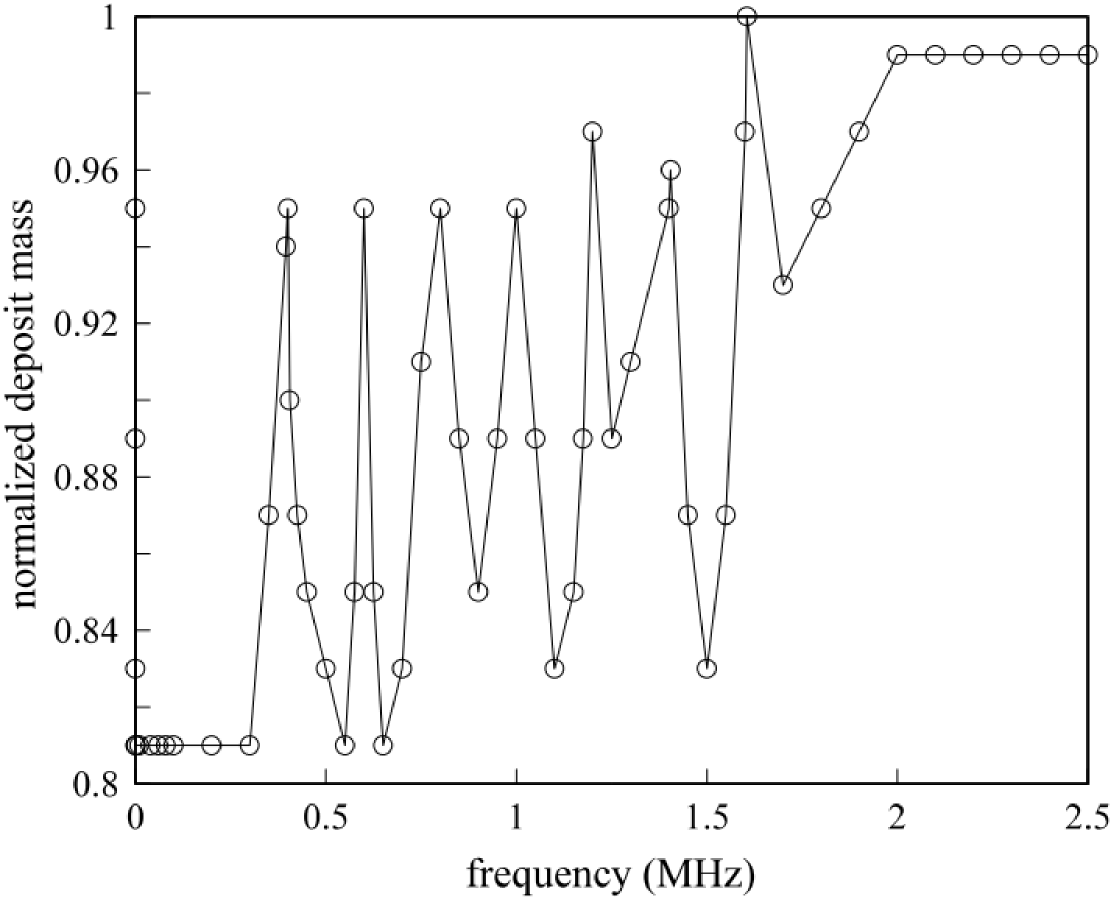

Figure 2. A plot of the normalized deposit mass vs. frequency for the Ni film at a solution temperature of 298 K. The solid line is drawn to help an eye.

As the electric circuit comprising the capacitance C, the inner electric resistance R_l, and the leakage resistance r is equivalent to the electric double layer in electrodeposition, we have the following equation [7] for the normalized mass m_a/m_e electrodeposited by the rectangular pulse current having the frequency f=1/2T where T is the current on-time (or current off-time),

$$\frac{m_a}{m_e} = \frac{1}{1+\frac{R_{ch}}{r}}\left[1+\left(1-\frac{R_l}{R_l+R_c}\right)\frac{1}{\alpha T}\frac{e^{-\alpha T}-1}{e^{-\alpha T}+1}\right], \quad (1)$$

where m_a is the actual deposited mass, m_e is the deposited mass expected for 100% current efficiency, $\alpha = [C(R_l + R_c)]^{-1}$, and $R_c = rR_{ch}/(r+R_{ch})$.

Taking $f \to \infty$, we have a constant value such as

$$\frac{m_a}{m_e} = \frac{1}{2\left(1+\frac{R_{ch}}{r}\right)}\left(1+\frac{R_l}{R_l+R_c}\right). \qquad (2)$$

The frequency-dependence of the deposited mass is due to the capacitative property of the electric double layer. Hence, the current that does not contribute to the formation of the nickel film passes through the electric double layer. As a result, the normalized deposited mass decreases with the frequency and approaches a constant value less than 1 according to Eq. (2). In Fig. 3, the solid curve best fitted to the experimental using Eq. (1) well describes the frequency-dependence of the deposited mass. The equivalent electric circuit model has no local maximum of normalized deposit mass for the frequency.

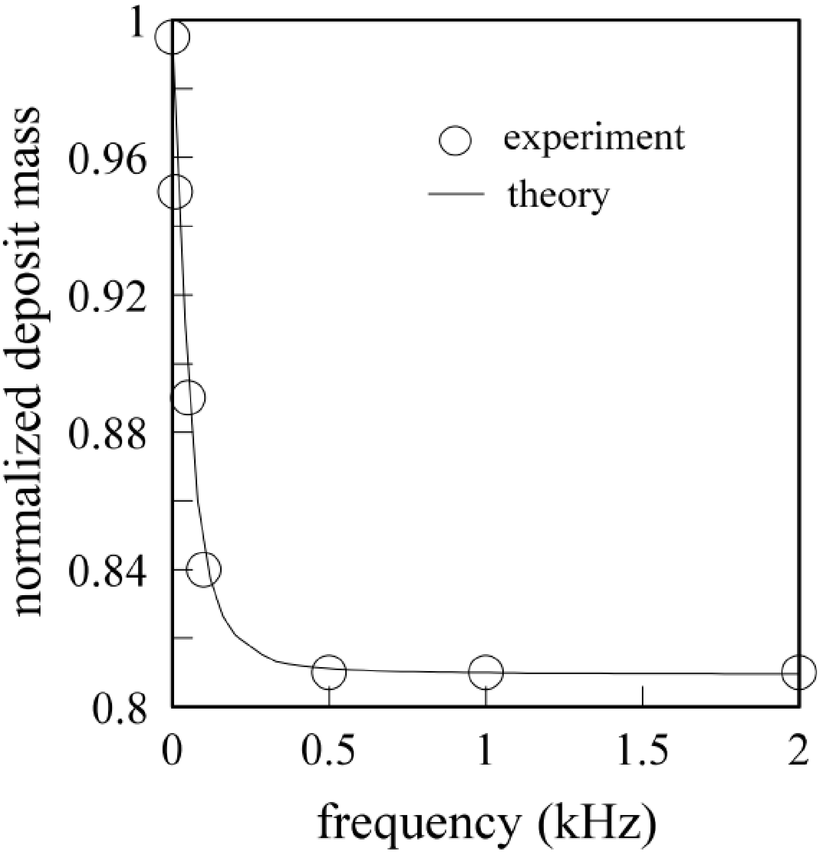

Figure 3. A plot of the normalized deposit mass vs. the low frequency for the Ni film at a solution temperature of 298 K. The open circles and solid curve show the measured deposit mass and the curve best fitted to the measured deposit mass using R_l=18.5 Ω, R_c=11 Ω, R_{ch}/r=5x10^{-3}, and C_s=95 μF.

However, as shown in Fig. 2, the normalized deposited mass starts deviating from the fixed value of 0.81 at frequencies higher than 0.3 MHz and has a local maximum value of 0.95 at a frequency of 0.4 MHz. Similarly, the normalized deposited mass has local maximum values of 0.95 at frequencies of 0.6, 0.8, and 1.0 MHz. The frequency at which the normalized deposited mass has a local maximum value is summarized in Table 1. As the deposited mass significantly increases at these frequencies in comparison with the saturated deposited mass, these frequencies may be called the resonant frequencies. The seven resonant frequencies are observed in the frequency range from 0.1 to 2.5 MHz.

Table 1. Resonant frequency and normalized deposited mass of the Ni electrodeposition in Figure 2.

Resonant frequency (MHz)	0.4	0.6	0.8	1.0	1.2	1.405	1.605
normalized deposit mass	0.95	0.95	0.95	0.95	0.97	0.96	1

In addition, the normalized deposit mass increases with frequencies over 1.7 MHz and indicates a constant value of 0.99 over a frequency of 2 MHz. In other words, the capacitative property of electric double layer explained using the equivalent electric circuit model seems to be lost. The origin of the capacitative property is due to the response of nickel sulfamate ions in or near the electric double layer to the alternative electric field. If the response to the alternative electric field means a change in polarity like a seesaw at the side of the electric double layer in the solution by the rotational motion of nickel sulfamate ions, no nickel sulfamate ion comprising one nickel ion and two sulfamate ions rotates at a frequency over 2 MHz. Hence, the current that passes through the electric double layer almost contributes to the formation of the Ni film at a frequency over 2 MHz. Hence, the normalized deposit mass shows a value of about 1.

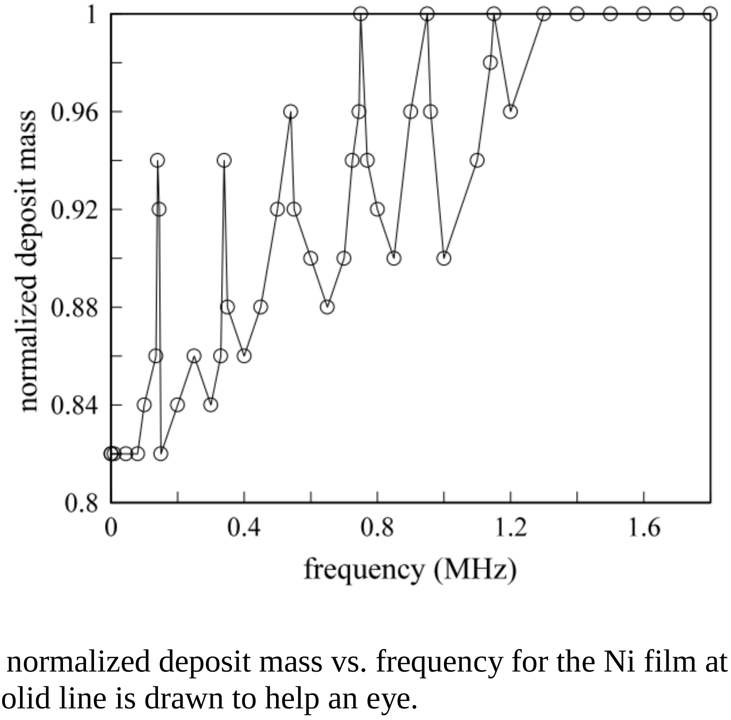

Figure 4. A plot of the normalized deposit mass vs. frequency for the Ni film at a solution temperature of 308 K. The solid line is drawn to help an eye.

The frequency spacing between the first and the second resonant frequency is 0.2 MHz as is evident from the data in Table 1. The average frequency spacing between the neighboring resonant frequencies approximately has a constant value of 0.202±0.002 MHz.

As is well known, the energy spacing of the electron, whose energy level is split by the crystal field, is in the range of visible light. Similarly, the energy spacings between the vibrational states and between the rotational states are in the ranges of IR and microwave frequencies, respectively. The frequency spacing that can be observed in Fig. 2 is extremely low because the electron in the electrode is not accelerated by light and microwaves, but by the applied electric potential whereby the transition energy level is small. In addition, using the current pulse with a megahertz-scale frequency, electrochemical reactions having a slow reaction time are screened.

Figure 4 shows the normalized mass of the Ni film electrodeposited at a solution temperature of 308K over a frequency range from 500 Hz to 1.8 MHz. The normalized deposit mass at a frequency less than 0.08 MHz has a constant value of 0.82 larger than that at a solution temperature of 298K. The first resonant deposition appears at a frequency of 0.14 MHz lower than that at a solution temperature of 298K. The remaining resonant frequencies in Fig. 4 are listed as 0.34, 0.54, 0.75, 0.95, and 1.15 MHz. The frequency spacing between the neighboring resonant frequencies is 0.202±0.004 MHz, which value is the same as that in a solution temperature of 298 K. In addition, the normalized deposit mass increases with the frequency and indicates a constant value of 1.0 over a frequency of 1.3 MHz less than that at a solution temperature of 298 K. An increase in temperature enhances a motion of water molecule in the solution. The response of nickel ion and sulfamate ions to the alternative electric field may be more disturbed by the movement of water molecule. Thus, the capacitative property is thought to be lost at a lower frequency.

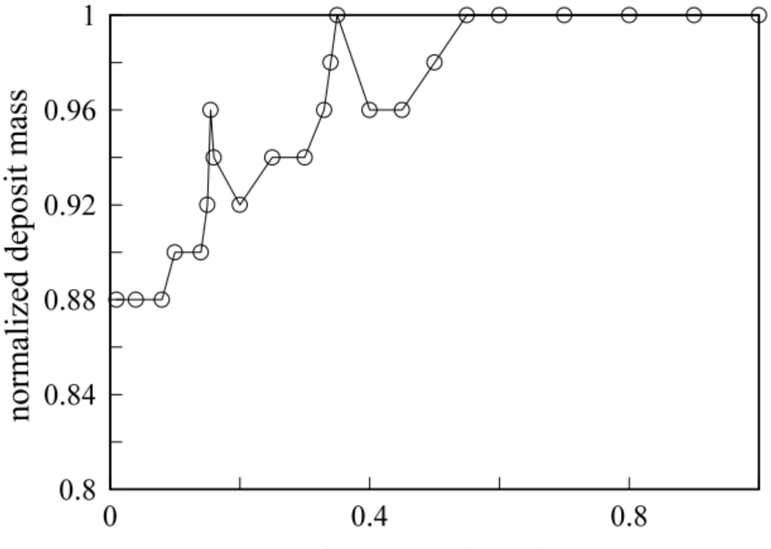

Figure 5. A plot of the normalized deposit mass vs. frequency for the Ni film at a solution temperature of 318 K. The solid line is drawn to help an eye.

Figure 5 shows the normalized mass of the Ni film electrodeposited at a solution temperature of 318K over a frequency of 10 kHz to 1.0 MHz. The normalized deposit mass at a frequency less than 0.08 MHz has a fixed value of 0.88 larger than that at a solution temperature of 298K. The first resonant deposition appears at a frequency of 0.155 MHz. The second resonant frequency is 0.35 MHz.

The frequency spacing between the two resonant frequencies is 0.195 MHz, which value is almost the same as that in a solution temperature of 298 K and 308 K. In addition, the normalized deposit mass increases with the frequency and indicates a constant value of 1.0 over a frequency of 0.5 MHz much less than that at a solution temperature of 298 K. The response of nickel ion and sulfamate ions to the alternative electric field may be more disturbed by the movement of water molecule. In a similar way, the capacitative property is thought to be lost at a much lower frequency.

The non capacitative frequency is defined as the minimum frequency at which the capacitative property is lost and the normalized deposit mass has a value of about 1. Figure 6 shows a plot of the non capacitative frequency vs. solution temperature. As the solution temperature increases, the non capacitative frequency decreases. An increase in the solution temperature accelerates the vibration and rotation of water molecules in the solution. As the result, a nickel ion and two sulfamate ions cannot rotate in a shorter time at a higher frequency. The non capacitative frequency shifts to a lower frequency with an increase with a solution temperature.

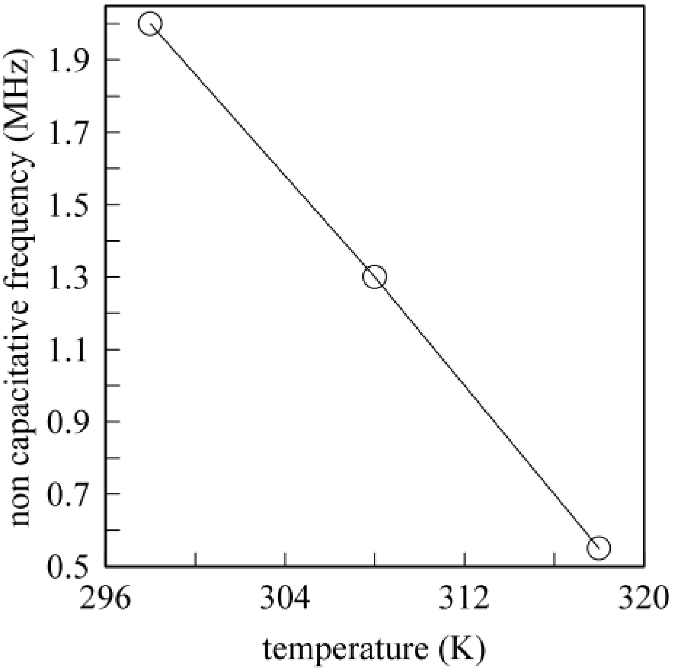

Figure 6. A plot of the non capacitative frequency vs. solution temperature.

At rotational energy levels, many resonant frequencies exist, and in particular, the energy spacing of the rotational energy for a linear molecule is constant [14-15]. The rotational energy level of Ni ions in sulfamate acid is experimentally and theoretically unknown [16-18]. Recently, the quantized rotational energy has been reported to play an important role in reactions at a low temperature [19]. As shown in Figs. 2, 4 and 5, the observed resonant frequency spacing has a characteristic similar to that of quantized rotational energy.

Here as a rough approximation, we consider the quantized rotational energy of a linear molecule comprising a single nickel ion and two sulfamate acid ions $(SO_3NH_2)^-$. The distance between the two ions, r can be estimated as follows: Using the quantized rotational energy level, E for the linear molecule, $\mathrm{E} = \frac{h^2}{8\pi^2 I} j(j+1)$ where h is the Planck's constant, $\mathrm{I} = \mu r^2$ is the moment of inertia, μ is the reduced mass, and j is the quantum number, the transition energy spacing from j=0 to j=1 becomes $\Delta\mathrm{E} = \hbar^2/I$. In this experiment, the typical current and potential between the electrode and the electric double layer were approximately I=20 mA and V=1 V. Using these values and the average frequency spacing Δf of 0.2 MHz, we have $\Delta\mathrm{E} = (IV/N)\cdot(1/\Delta f)\cdot 2 = 1.602x10^{-24} J$ per two electrons where N is the number of electron. Substituting the reduced mass μ of 3.192x 10^{-25} kg into $\hbar^2/\mu r^2 = \Delta E$, we obtain r of 0.92 nm, which is considered reasonable in comparison with the ion size of sulfamate ion, 0.3 nm [20].

4. CONCLUSIONS

In current pulse electrodeposition at a frequency of 10 Hz to 2.5 MHz, the resonant frequency for the deposit mass of Ni is observed. The average frequency spacing between the neighboring resonant frequencies in nickel electrodeposition approximately has a constant value of 0.2 MHz. The observed resonant frequency spacing has a characteristic similar to the quantized rotational energy and the distance between a nickel ion and a sulfamate ion is estimated at 1.1 nm. The non capacitative frequency at which the capacitative property is lost and the normalized deposit mass has a value of about 1 is observed and shown to decrease with the solution temperature.

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