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Faraday instabilities leading to electrochemomechanical generation of sub-μA ACupon application of DC voltage across free standing oil-water interfaces

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***Abstract*—In this article, we report the generation of alternating current by application of constant and ramping DC voltages across oil-water interfaces. The work reported here can be broadly divided into two parts depending on the shapes of oil-water interfaces i.e. flattened and curved. In the first part, an alternating current of ~100 nA (amplitude)was generated by applying a constant DC voltage of -3V& above across a free standing and flattened oil-water interface.In another part, an alternating current of ~150 nA (amplitude) was generated by applying a ramping up DC voltage starting from -5V to 5V, then again ramping back down to -5V for the free standing and curved interface. The suggested qualitative mechanism that engenders such a phenomenon includes the oil-water interface acting like a membrane. This membrane oscillates due to the electrophoretic movement of ions present in aqueous phase by application of a DC voltage across the interface.This electrophoretic movement of ions across oil-water interfaces causes the Faraday instabilities leading to oscillations of the said interface.This method could also be used to study the stress levels in the interfacial films between two immiscible liquids. It explores more-than-Moore's paradigm by finding a substitute to a conventional alternator/inverter that generates alternating current upon applying DC voltage input. This work would be of substantial interest to researchers exploring alternatives to conventional AC generators that can be used in liquid environments and in the design of novel integrated circuits that could be used for unconventional computing applications.**

***Index Terms*— actuator, alternator, electrochemomechanical, inverter, more-than-Moore, oil-water interface, oscillator, pH, unconventional computing**

I. Introduction

Oil-water (OW) interfaces display very interesting properties at different pH values. Normally, we find these interfaces to be curved in nature. Electrochemomechanical transitions of such interfaces at varying pH have been studied, showing that flattening of OW interfaces take place in extreme alkaline conditions [1]. In extreme alkaline conditions, these interfaces flatten due to the ionization of constituent fatty-acid molecules of the oil. Due to the ionization of oil's constituents, there is a formation of an interfacial free standing membrane of molecular thickness between oil phase and aqueous phase (Figure 1).

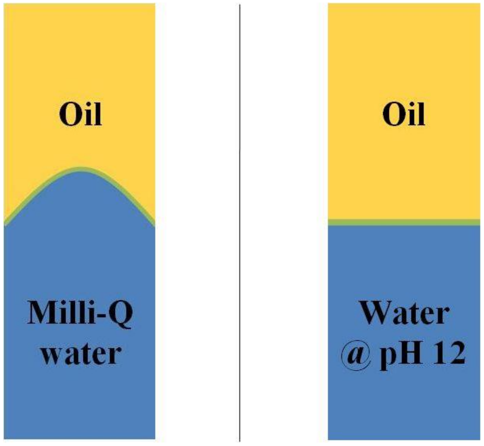

Fig. 1 Schematic of different oil-water interfaces, left panel showing the curved interface whereas the right panel showing the flattened interface. The molecularly thick interface is marked green.

Different freestanding membranes have been demonstrated as particle separators [2] and power generators [3] based on the elastic properties of the said membranes.Ion transfer between two immiscible liquids, water and nitrobenzene (approximating the oil phase), was studied with varying potential demonstrating the electrically rectifying heterojunction like behavior [4].

Alternating current generators are commonly known as alternators/inverters [5, 6]. Here, we report the alternating behaviors of curved and flattened OW interfaces by applying a DC voltage across it. In binary fluid systems, Faraday instabilities have been reported for binary immiscible fluids. If the two immiscible fluids are assumed to be inviscid, the perpendicular oscillations of such an interface can be given by equations (1a)-(1c) as follows:

$$\frac{d^2Y}{dt^2} + \left(p - 2q\cos(2t)\right)Y = 0 \tag{1a}$$

$$p = \frac{(\rho_1 - \rho_2)gk - \gamma k^3}{\rho_1 \coth(kh_1) + \rho_2 \coth(kh_2)} \tag{1b}$$

$$q = \frac{(\rho_1 - \rho_2)A\omega^2}{2\{(\rho_1 \coth(kh_1) + \rho_2 \coth(kh_2)\}} \tag{1c}$$

where, Y: wave response amplitude, t: time, p: square of natural wave frequency of the binary Faraday system, ρ_1, ρ_2: densities of two immiscible fluids comprising the binary system, γ: surface tension between the two immiscible fluids, k: wavenumber,h_1, h_2: heights of two immiscible fluids comprising the binary system,A: amplitude of applied force on OW interface, ω: frequency of the applied force on OW interface and q: parametric amplitude. Since the applied impulse on the interface causing the OW interface to generate an AC current is a constant DC voltage, ω would be reduced to zero. Thus for the sake of this work, the q term would not play any role in the generation of Faraday waves in the OW interface. The currents thus generated are because of varying wave response amplitudes, Y, and the ideal stable interfacial oscillations would lead to alternating amplitudes thus engendering alternating currents, as discussed further in the paper.

Mustard oil was used as the oil phase in this work. Flattening of OW interface was done by increasing the pH of aqueous phase to 12 [1]. This happens due to the ionization of entire fatty acid constituents of mustard oil, short & long chain as well as mono-unsaturated & poly-unsaturated.One of the major mono-unsaturated fatty acid constituent of mustard oil is erucic acid has an estimated pK_a value of 4.7. This means that even at neutral pH (when the interface is curved), some of the fatty acids (i.e. erucic acid and the ones whose pK_a values are lesser than 7) are ionized and therefore form a molecularly thick membrane.This molecularly thick membrane would oscillate due to the electrophoretic mobility of ions present in the aqueous phase. This oscillatory motion would cause the electrochemical current to fluctuate, resulting in the alternator/inverter like behavior of free standing and flattened/curved OW interfaces. A detailed discussion regarding the same is done further in the article.

II. MATERIALS & METHODS

Chemical: For the first part of the work, the aqueous phase at pH 12 was prepared by serially diluting the stock solution of NaOH (1M). The stock solution of NaOH was prepared by dissolving 400 mg of NaOH pellets (Himedia, MB095) in 10 ml of Milli-Q water. For the oil phase, commercially available mustard oil was used in this work. 0.5 ml of oil was poured over 1 ml of aqueous phase at pH 12 in a 2 ml Tarsons eppendorf tube to form the flattened OW interface.For the second part of the work, 0.5 ml of oil was poured over 1 ml of Milli-Q water to form the curved OW interface.

Electrical: The two-terminal electrical measurements were done using a makeshift device with the metal (iron) paper pins used as electrodes, inserted in the eppendorf tube,as shown in Figure 2.

Fig. 2 Experimental setups for the two-terminal I-Vmeasurements in DC modeare shown. The experiments were conducted for different oil-water interfacial areas, as indicated.

The electrical measurements were done using a single channel Keysight B2901A Precision Source/Measure Unit in DC mode.Data acquisition was done using *Keysight B2900A Quick IV Measurement Software, Version 4.1.1821.3680* [7]. All the control parameters were set using the software's graphical user interface (GUI). A potential of -10 V was applied with a compliance of 0.01 A for the flattened OW interface. For the curved OW interface, the DC potential was linearly varied from -5V to 5V & then back to -5V. In both these cases, 1000 data points were collected to study the behavior of the interfaces more accurately in comparison to lesser number of data points. The current range was limited to 1 μA and the measure delay was 0.5 seconds.In advanced settings, the capacitance mode was kept normal, filter in ON mode, time constant was 5×10^{-6}, thresholdwas kept at 90%, and source& measure wait gains were kept at 1 while the source & measure wait offsets were kept at 0 s. Rest all the parameters were kept in their default/auto settings.

III. RESULTS & DISCUSSION

A. Flattened OW Interface

The two-terminal I-Vmeasurements were carried out in DC mode, using the experimental setup as shown in figure 2. The resulting trends of current-time are shown in figure 3, as follows:

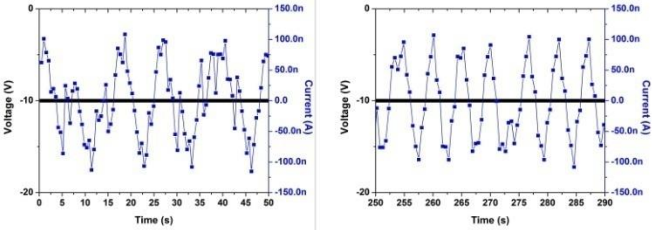

Fig. 3 For flattened OW interfaces, current-time trends (in blue) shown for first 50 seconds from the start of the experiment depict a noisy behavior (left panel) & 250-290 seconds from the start of the experiment depict a periodic behavior (right panel).

Since the mobile charge carrier in this case is OH$^-$ that is present in the aqueous phase, its electrophoretic movement away from the negative terminal (aqueous phase is at -10 V w.r.t. the oil phase) would cause a bending of the OW interfacial membrane towards the oil phase (stage I). An extensive discussion of the ion-impingement induced bending of OW interface is done in reference [8]. The said bending happens because of the hydrophilic nature of the OH$^-$ ion, which would preferably be surrounded by water molecules and would have great difficulty to instantaneously move into the hydrophobic phase. The bending of the membrane towards the oil phase would generate a positive electrochemical current. While this electrophoretic movement of OH$^-$ ions induced bending takes place, the fatty acid molecules in the oil would get completely ionized due to interactions with the impinging OH$^-$ ions at extremely alkaline conditions (i.e. pH 12), since the primary constituents of cooking oil are long chain unsaturated fatty acids with their pK$_a$ values ranging from 8-11 [9]. Such bending would continue till the point when it could go no further and the direction of movement of the membrane would reverse i.e. towards the aqueous phase (stage

II). The schematic of the electrophoretic oscillations upon application of negative potential to the aqueous phase is shown in figure 4, as follows:

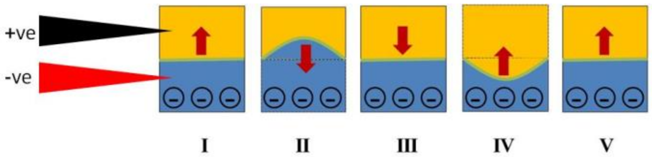

Fig. 4 Electrophoretic movement of negatively charged OH$^-$ ions, away from the negative electrode on the aqueous side leads to the generation of positive electrochemical current; whereas the movement of OH$^-$ ions towards the negative electrode leads to the generation of negative electrochemical current. Different stages (I-V) of interfacial OW membrane have been depicted in the figure.

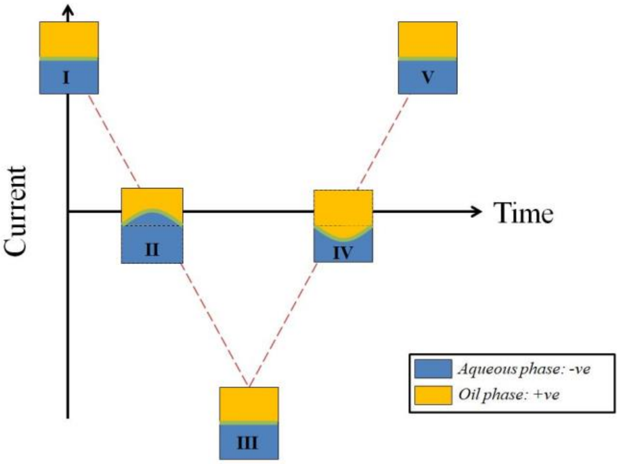

Fig. 5 Mechanism of generation of alternating current due to the bending of OW interfacial membrane is shown. Aqueous phase is at a negative potential of -10V w.r.t to the oil phase, rendering the oil phase to be at a relatively positive bias.

When the movement of OW membrane is in the opposite direction i.e. towards the aqueous phase, it would bring along ionized fatty acid molecules rendering the slight golden color (of the oil) to the aqueous phase. The same can be seen in figure 2. The movement of the OW membrane towards the aqueous phase, pushing the OH$^-$ ions towards the negative potential would generate a negative current till the maxima of bending in the aqueous phase is reached (stage III). After this stage, the OW membrane would again start moving towards the oil phase, pushing the OH$^-$ ions away from the negative potential, thus generating a positive current (stages IV & V). It is evident from the schematic shown in figures4& 5, depicting the bending phenomenon, that stage V is mechanically analogous to stage I of the OW interface. The vibrations of the free standing OW interfacial membranes could be modelled using the methods described in reference [10-14]. Such periodic movements of OW membrane would therefore generate an alternating electrochemical current of the frequency same as that of oscillating membrane.The same has been shown in figure 3, left panel of which shows high noise levels at the start of the experiment whereas the right panel shows the periodic oscillatory current owing to the oscillations of the OW membrane (after ~250 s of the start of the experiment).

B. Curved OW Interface

The curved OW interface was obtained owing to the lower pH value of the aqueous phase [1]. To generate an alternating current by applying a DC voltage input across such an interface, we applied linearly ramping up DC voltage inputs ranging from -5V to 5V, and then decreasing it back to -5V. For the first 250 (out of 1000) recorded data points, till the aqueous phase was at a negative bias w.r.t. the oil phase, the current-time trend did not follow any pattern, as seen in the top-left panel of figure 6.

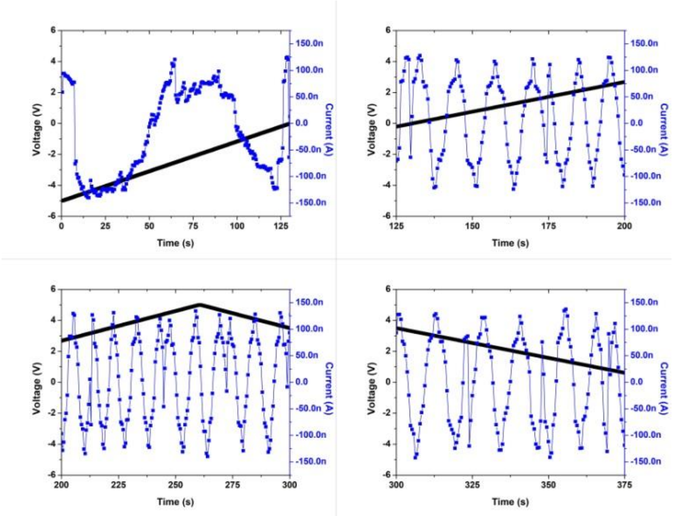

Fig. 6 For curved OW interface, current-time trends (in blue) show a totally random trend for the first quarter of the recorded measurements. After that, a periodic behavior is observed. The voltage variation is also shown (in black). The AC frequency is ~ 0.08 Hz till 360 s, which further increased to ~ 0.12 Hz.

When the aqueous phase became positive w.r.t. the oil phase, there was a sudden transition observed in the dynamic current behavior. While it was totally random behavior in the first quarter of the recorded measurements, the currents suddenly became periodic (frequency ~ 0.08 Hz) and alternating with amplitude of ~ 150 nA. The random dynamic behavior of the currents at the very onset of the measurements could be explained by the lack of mobile negative charge carriers in the aqueous phase, when it was at a negative bias w.r.t. the oil phase. As the bias of the aqueous phase turned positive w.r.t. the oil phase, the ionized erucic acid and other fatty acids (at the curved OW interface) with pKa values lesser than 7 having a negative chargeat neutral pH, would start to electrophoretically migrate towards the aqueous phase. This electrophoretic migration would lead to the intermittent decrease in the curvature of the already curved OW interfacial membrane. This intermittent behavior would lead to the oscillation of the curved OW membrane and pushing of the negatively charged, ionized erucic acid molecules into the aqueous phase.

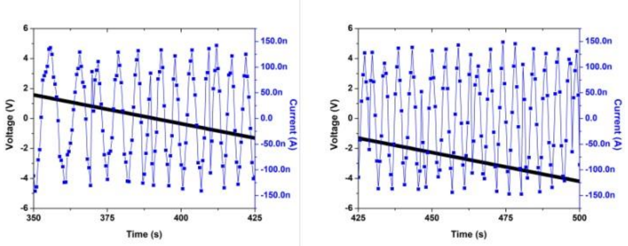

Fig. 7 An increase in the AC frequency is shown, from ~ 0.12 Hz (from 360 s to 390 s) to ~ 0.16 Hz (395 s onwards).

An increase in the AC frequency from 0.08 Hz to 0.12 Hz in the timeframe 360 s to 390 s can be attributed to the incipientexpansion of OW interfacial membrane due to high accumulation of negatively charged, ionized erucic acid molecules (hydrophobic in nature).This expansion of curved OW membrane would happen because the applied DC bias on the aqueous side becomes lesser than the required potential to pull the membrane towards it. Effectively, this marks the start of the oscillation of curved OW membrane due to repulsive electrostatic forces, switching from the attractive electrostatic forces resulting in gradual increase of the generated AC frequency.Till the time the linearly varying DC input reaches the zero value, substantial amount of negative charge carriers in the form of ionized erucic acid has already been accumulated in the aqueous phase. Thus, when the DC voltage input traverses back putting the aqueous phase into the negative bias, the frequency of the generated alternating current is predicted to increase because of the abundant mobile charge carriers in the aqueous phase. The same phenomenon is also seen in our experiments, as shown in figure 7, increasing the AC frequency to ~ 0.16 Hz.. At this point, the negative bias on the aqueous side would push the negatively charged erucic acid ions accumulated in water towards the oil phase as well as electrostatically push away the negatively charged OW membrane towards the oil phase. The phenomenon, as discussed above in context of curved OW interface, is shown schematically in figure 8. We propose that this alternating current generation can be attributed to the periodic oscillation of pre-stressed, curved OW interfacial membrane. This schematic discussed is analogous to the one discussed in figure 5 i.e. mechanically analogous oscillatory stages would show same current levels. Increasing interfacial areas between oil-water led to decreasing amplitude of the alternating currents.

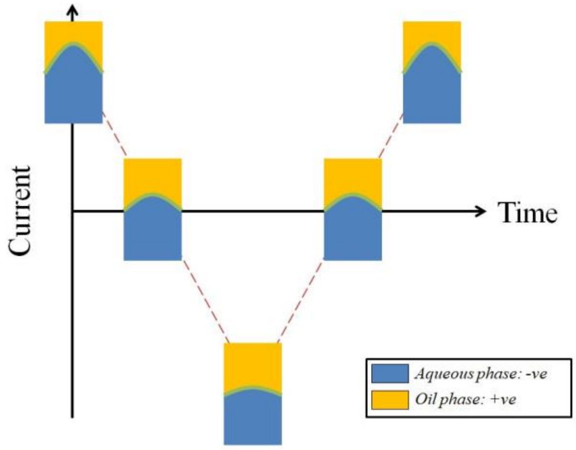

Fig. 8 Mechanism of alternating current generation via curved OW interfaces due to periodic reduction in interfacial curvature is schematically shown. The interfacial membrane is pre-stressed in comparison to the flattened interfacial membrane, leading to lesser frequency of alternating current.

The amplitudes of the alternating currents showed a decline with increasing OW interfacial areas. This could be explained by the lesser amplitude of interfacial membrane fluctuation due to an increased interfacial area. However, the trend of alternating current production remains the same (with same frequency). The measurements pertaining to varying input DC voltages and interfacial areas are reported in the supplementary information of this manuscript.

IV. CONCLUSION

We have demonstrated an electrochemomechanical mode of generating alternating current for a given DC voltage input for two types of OW interfaces, flattened and curved, due to Faraday instabilities. Advanced analyses for such OW interfacial oscillations are beyond the scope of the current work. Extensive theoretical treatise of Faraday instabilities due to perpendicular forces &electric fields can be found in reference [15, 16]. For the flattened OW interface, a constant DC bias was required to generate an alternating behavior whereas for the curved OW interface, a linearly ramping DC bias was required for the same purpose. Such alternating behavior of OW interfaces could be explained qualitatively by the periodic oscillations of the OW interfaces due to impingement of ions from the aqueous phase (for the flattened interface) and electrophoretic movement of the charged OW interface & ions in aqueous phase (for the curved interface). However such qualitative explanation for the observed phenomena could only be applicable in restricted areas of oil-water interfaces.Our experimental setup is analogous to an alternator or an electronic inverter that is used to generate alternating current using a DC voltage input. This work paves the way towards the more-than-Moore’s paradigm by exploring alternatives for conventional electronic components. The device setup discussed in this work is of potential use in a liquid environment, which would normally limit the performance of conventional electronic devices. The method discussed in this paper could also find potential applications in determining the mechanical behavior of pre-stressed films between two immiscible fluids by studying the trends of current oscillations.This paper would be of immense interest to the researchers working towards exploring novel current generatorsand in designing novel integrated circuits that might be useful for unconventional computing applications.

V. AUTHOR CONTRIBUTIONS

A.K. conceived the idea. A.K., A.G., A.P., D.B. & A.K.P. performed the experiments. A.K., A.G., A.P., D.B., A.K.P.& S.R.R.analysed the data and wrote the manuscript.

VI. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Supplementary Information for

Faraday instabilities leading to electrochemomechanical generation of sub-μA AC upon application of DC voltage across free standing oil-water interfaces

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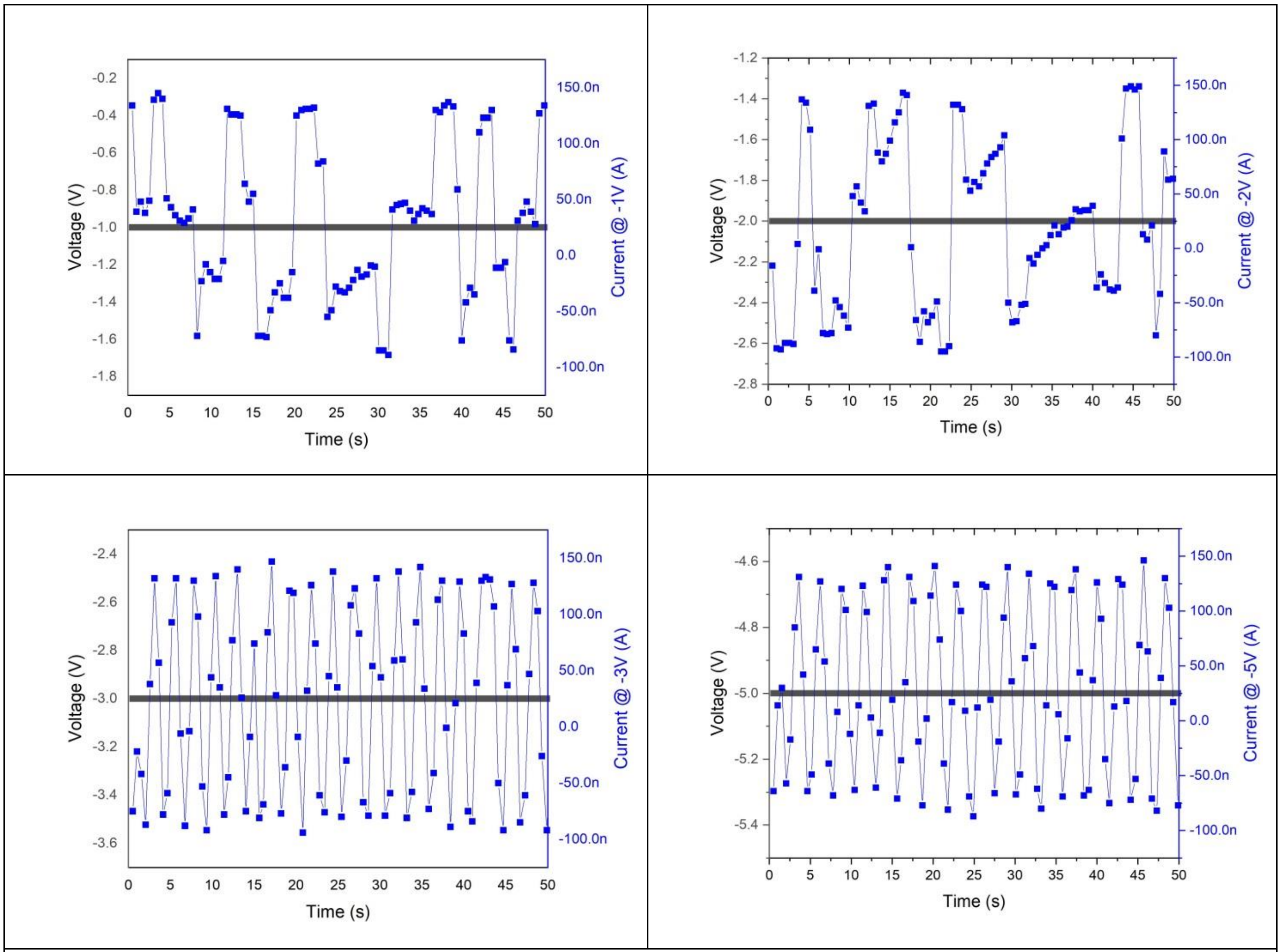
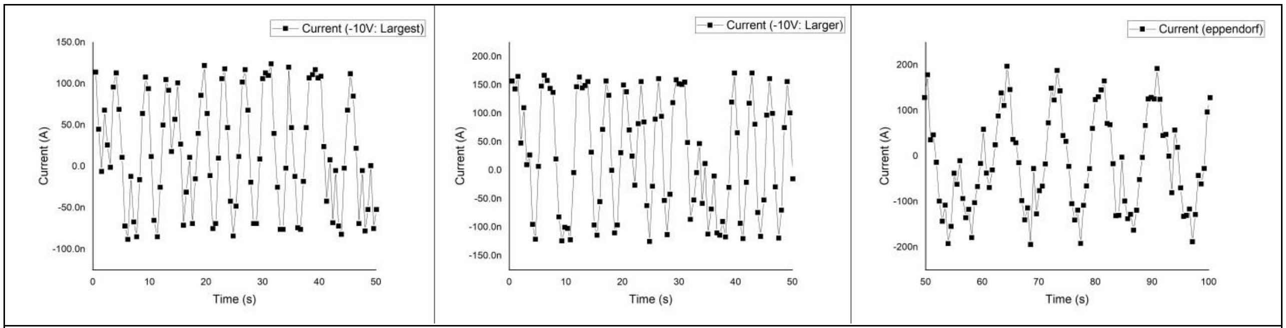


Irregular current patterns are seen for input DC voltages of -1V & -2V. However, when the input voltages are increased to -3V & beyond, a periodic alternating current is obtained.



Current variations for varying interfacial diameters depicting the gradual decrease in current amplitudes with increasing areas