



Influence of an active vibration isolator and electrochemical cell design on electrochemical measurements to minimize natural convection



Kyungsoon Park^{a,1}, Eunsung Kim^{a,1}, Jun Hui Park^{b,*}, Seongpil Hwang^{a,*}

^a Department of Advanced Materials Chemistry, Korea University, Sejong 30019, Republic of Korea

^b Department of Chemistry Education and Institute of Fusion Science, Chonbuk National University, Jeonju 54896, Republic of Korea

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ABSTRACT

The influence of an active vibration isolator (AVI) and electrochemical cell design on natural convection was investigated. The natural convection of an electrolyte caused by external vibrations and acoustic sounds is reduced by both an AVI and an acoustic enclosure. Slow scan voltammetry with an AVI shows a reproducible and predictable diffusion-controlled current down to 0.4 mV/s. Reducing the distance between the working electrode and the glass wall also has a considerable effect on the voltammetric signal.

1. Introduction

The voltammetric [1] or chronoamperometric [2] response predicted by the Randles–Sevcik equation, Shoup and Szabo approximation [3] or the Cottrell equation [4] is the fundamental basis for modern electrochemistry, which assumes diffusional mass transport without convection or migration. This hypothesis is valid in conventional electrochemical experiments due to negligible migration by the excess supporting electrolyte and the stationary electrode/electrolyte. For well-defined forced convection, the Koutecky-Levich equation [5] for a rotating disk electrode (RDE) [6] and the theory of electrochemical flow cells [7,8] offer an insight into electrochemical behaviour. Over a longer time scale, however, for example when using a slow scan rate or a long electrolysis period, uncontrollable factors generate motion in the solution, called natural convection, which causes a deviation from theoretical results as well as poor reproducibility. Possible contributors to this motion include:

- (1) The density gradient during electrolysis can drive the gravity force, resulting in currents dependent on the electrode direction [9]. The Compton group reported a quantitative analysis of this effect, based on a simulation [10].
- (2) Thermal convection caused by the heat of a reaction might influence convection. However, a recent simulation showed a negligible thermal effect on convection [11].
- (3) Mechanical vibrations, the movement of air and the cell configuration might induce convection. The Amatore group developed a

model for this effect in which the thickness of the limiting diffusion layer is an important parameter [12].

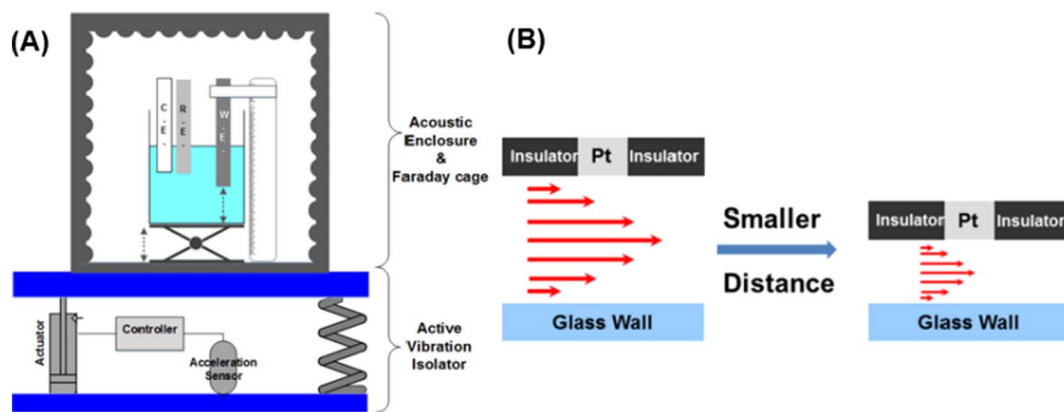
Previous work has been focused on the origin of natural convection, with only a few reports aiming to minimize natural convection in electrochemical experiments. Electrochemical behaviour over longer time scales has attracted increasing interest from researchers in reaction mechanisms, enhanced sensitivity, and higher resolution scanning electrochemical microscopy (SECM) [13], where unprecedented movement control in experiments is required. Two of the causes of natural convection, mechanical vibration and acoustic motion, can be minimized under well-controlled conditions. Recently, the Aoki group reduced mechanical convection through enhanced viscosity by adding a gelling agent [14]. Our group used a hydrogel to help reduce the motion in a previous study [15]. To the best of our knowledge, however, there have been no attempts to minimize the mechanical motion in a typical electrochemical cell in the absence of additional chemicals which may influence the electrochemistry at the interface or the mass transport within the solution.

The objective of our work was to minimize the vibrational and acoustic motion of the electrolyte in natural convection. Firstly, an active vibration isolator (AVI) was used to control and reduce the vibration precisely. While a passive vibration isolation system such as an optical table can reduce vibrations above 10 Hz, AVI can work down to 0.5 Hz with enhanced performance. It can cancel out external vibrations using accelerometer-controlled actuators, and is used in atomic force microscopes (AFM), interferometers [16] and other devices.

* Corresponding authors.

E-mail addresses: echem@jbnu.ac.kr (J.H. Park), sphwang@korea.ac.kr (S. Hwang).

¹ Equal contribution.



Scheme 1. Illustrations of (A) the setup with AVI and acoustic enclosure in place and (B) velocity distribution of laminar flow. The speeds at stationary plates are zero. The red arrows represent the velocity of the electrolyte parallel to the plates. (For interpretation of the references to color in this scheme legend, the reader is referred to the web version of this article.)

Secondly, an acoustic enclosure served as a faraday cage to reduce acoustic vibrations. Thick (~10 mm) plates of metal were assembled into a box, and soundproof foam panels covered the inside, as shown in Scheme 1(A). A disk electrode and 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ aqueous electrolyte were used to keep the density-gradient convection low [10]. Thirdly, the distance of the disk electrode from the wall of the glassware was adjusted. We speculate that the velocity of the laminar flow parallel to the plates in the middle of the gap is slower when the gap is smaller, as shown in Scheme 1(B). Thus, natural convection could be minimized by decreasing the gap between the disk electrode and the glass wall. The precision with which the distance is controlled is of the order of mm, using the simple setup shown in Scheme 1(A).

2. Experimental

All chemicals (obtained from Aldrich) were used as received. The polished Pt disk electrode (1.6 mm in diameter, BAS Inc) was fixed vertically with a ruler (Scheme 1A) within a homemade faraday cage/acoustic enclosure on an active vibration isolator (DVIA-T67, Daeil Systems, Korea). The gap distance was adjusted using a support jack. The aqueous electrolyte contained 1 mM $\text{Fe}(\text{CN})_6^{4-}$ and 0.5 M KCl in all experiments. Electrochemical experiments were performed with a CHI 730E after 1 h to allow the natural convection to settle down. A Pt wire and Ag/AgCl (sat'd KCl) served as the counter and reference electrode, respectively. To investigate the effect of vibration, an electric toothbrush (Oral-B DB4010, Braun) acted as a vibration source, and the vibrations were measured by a VM-6360 vibration meter (Landtek Instruments, China).

3. Results and discussion

Firstly the effect of the gap size in the electrochemical cell was investigated. The Pt disk electrode was positioned at 0.5, 1 or 2 mm from the wall of the glass beaker. Cyclic voltammetry was performed in the absence of both the AVI and the acoustic enclosure. Fig. 1(A) shows the cyclic voltammograms (CVs) obtained with a gap of 2 mm. While conventional CVs were observed at a scan rate over 3 mV/s, the CVs observed with a scan rate under 1 mV/s showed (1) a sigmoidal shape, (2) very poor reproducibility in a pseudo-steady-state current, and (3) independence of the scan rate, assumed to be caused by natural convection [12]. With a smaller gap of 1 mm, predictable behaviour was observed with scan rates as low as 0.7 mV/s. At a scan rate of 0.5 mV/s, however, a fluctuating pseudo steady-state current was observed (Fig. 1(B)). CVs taken with a gap of 0.5 mm, shown in Fig. 1(C), show conventional CVs for scan rates down to 0.7 mV/s and then change to a sigmoidal shape at 0.5 mV/s. The peak currents depend on $v^{1/2}$, as predicted by the Randles-Sevcik's equation, down to 0.7 mV/s,

indicating the absence of natural convection. The natural convection is reduced by the disk electrode approaching the glass wall, probably due to the slower speed of the laminar flow as shown in Scheme 1(B). The higher ratio of the stationary area over the electrolyte volume within the thin layer between the electrode and the wall may cause higher frictional forces.

To study the effect of vibration on the electrochemistry, the CVs were measured using electrical toothbrushes as a vibration source. These were positioned near the electrochemical cell; the amplitude of the vibration could be adjusted by changing the number of toothbrushes and their distance from the cell. A vibration meter in acceleration mode measured the amplitude of the vibration in the electrochemical cell with a 1 mm gap. Fig. 2(A) and (B) show the CVs measured with vibrations of 1 and 3 m/s^2 , respectively. The CV taken at a scan rate of 0.7 mV/s appears to be more sigmoidal in shape than the CVs recorded at the same scan rate in Fig. 1(B) and Fig. 3(A). The plots of $v^{1/2}$ vs I_p shown in the insets also demonstrate that the deviation from the linear relationship starts at ca. 0.7 mV/s and that the deviation at 0.5 mV/s increases from 0.54 μA at 1 m/s^2 to 0.63 μA at 3 m/s^2 . A further investigation might be helpful to understand the effect of the vibration on the electrochemistry, which is beyond the scope of this work. Overall, the CVs recorded at a slower scan rate are more affected by the external vibration, and the shorter distance from the wall reduces natural convection.

Next, we investigated the effect of the acoustic enclosure and AVI at 1 and 0.5 mm gaps from the wall. Fig. 3(A) shows the conventional CV shape down to a scan rate of 0.5 mV/s, where the effect of the natural convection is inevitable in the absence of the AVI as shown in Fig. 1(B). Although the CVs show irreproducible and higher quasi-steady state currents below 0.5 mV/s, AVI reduces the effect of the natural convection. With a shorter distance of 0.5 mm, the CVs seem to be more reproducible, even at slow scan rates (Fig. 3(B)). The plot of the peak currents versus $v^{1/2}$ at the 0.5 mm gap (Fig. 3(C)) shows the predicted linear behaviour down to ca. 0.4 mV/s. At slower scan rates of 0.2 mV/s and 0.1 mV/s, the peak currents are higher than the predicted values. It is also worth mentioning that the quasi-steady-state currents at slow scan rates seem to be random and independent of the scan rates. Two effects may influence the voltammograms. Firstly, the edge effect of diffusion is not negligible at slow scan rates because both the thickness and shape of the diffusion layer on a macroelectrode are similar to radial diffusion on an ultramicroelectrode. Assuming that the diffusion coefficient of ferrocyanide is $0.67 \times 10^{-5} \text{ cm}^2/\text{s}$ [17], the thicknesses of the diffusion layers calculated from the square root of $D \times t$ are ca. 0.82, 1.16, and 1.42 mm for 1000, 2000 and 3000 s, respectively. These thicknesses are comparable with the 1.6 mm diameter of the disk electrode, indicating that radial diffusion must be considered similar to that of an ultramicroelectrode. Secondly, the thickness of the diffusion

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