

# Reply to Comments on the Article "An Electrochemical Impedance Measurement Techniques Employing Fourier Transform"

SIR: In his comments on our newly developed impedance measurement technique using Fourier Transform,<sup>1</sup> Lasia states that the technique does not contain any information in a low-frequency region, because it is obtained from an extrapolation of the data obtained up to  $(n_0 + 1)\Delta t$ , where  $n_0 + 1$  is the number of points sampled, and  $\Delta t$  is the sampling time. This is not true, because the technique is based on a principle in which a Dirac  $\delta$  function, which is composed of AC voltages of *all* of frequencies ranging from infinitely high to infinitely low frequencies (almost dc level) of the same magnitude and phase,<sup>2</sup> is applied to the electrode/electrolyte interface as an excitation source, and the response current resulting thereof is detected and decomposed back into each frequency component by means of Fourier transform (FT). It is similar to a concept used in today's spectrophotometers in which a white light source is used for a sample, followed by decomposing the response signal into each wavelength component using a grating, and detecting them with a photodiode array or a charge-coupled detector. In our measurements, however, an integrated form of the Dirac  $\delta$  function is applied instead, and the derivative current signal is obtained before decomposing it into each AC current component, because it is very difficult to generate and directly apply the Dirac  $\delta$  function by known electronic circuits. In doing so, we took advantage of another theorem,<sup>3</sup> which states that for a linear system responding with a function  $y$  for an input function  $x$ , an input of an integrated or derivative form of the function  $x$  gives a response function of integrated or derivative form of  $y$ .

Although the Dirac  $\delta$  function contains *all* of the frequencies, its duration is *very short*, almost 0 in fact, which causes confusion on the part of many investigators. That a signal contains a low frequency component does not necessarily mean that it should last as long as  $1/f$ , where  $f$  is the lowest frequency, as most people understand it as a sampling theorem. Now, let us examine a case in which a signal having a form of the Dirac  $\delta$  function (i.e., an impulse) with a total sampling time of 1 ms is acquired in an experiment, because we *know* the signal is 0

outside the sampling time from the definition of the Dirac  $\delta$  function. The data were obtained at a sampling frequency of 1 MHz, for example. When this signal is Fourier transformed into the frequency domain, would the decomposed, sinusoidal signals not contain AC waves in a lower frequency region than 1 kHz, because the total sampling time is only 1 ms? This question can be rephrased: We *know* addition (or integration) of all of the AC waves of different frequencies ranging from infinitely high to almost 0 frequency gives a Dirac  $\delta$  function; the Fourier transform of the resulting Dirac  $\delta$  function *must* lead back to the original AC waves! There is no other way around this, because these conversion processes *must* be reversible in both directions.<sup>4</sup> As a final point, would the data points beyond the time region, where the Dirac  $\delta$  function decays to 0, be helpful in restoring the AC waves? This question is rather well-addressed in a textbook, which explains the difference between the digital/fast FT (DFT/FFT) and discrete-time FT (DTFT).<sup>5</sup> The latter (DTFT) is the algorithm we used. Investigators are so much used to the DFT/FFT methods in which the theorem as to the sampling frequency is applicable and, thus, overlook what DTFT can do for a system like the one we described in our work.

In addition, we did not take the data assuming  $i = 0$  at  $t > (n_0 + 1)\Delta t$  (by the way,  $\Delta t$  is not the sampling time, but the sampling interval). Instead, we stopped taking the data when the derivative of the current becomes 0, which is the time when the response signal to the Dirac  $\delta$  function becomes 0. In an ideal situation, there is no information outside this range, as was explained above; what we need is just to recover the Dirac  $\delta$  function current. Thus, our method does *not* extrapolate the data into the low-frequency region, but the data at low frequencies are contained in the impulse we obtained by taking the derivative of the current, except for the information on the Warburg component, which is caused by the difference in the phase between the applied ac wave and the mass transport (see below). The current impulse we obtained here is actually a white spectrum containing data at all of the frequencies. In fact, we did include the data outside this range for a different reason, that is, to increase the frequency resolution of the data.

The Warburg impedance is observed at low frequencies in electrochemical experiments, because the mass transport cannot catch up with the ac potential change due to the sluggish diffusion process. Thus, no Warburg component is seen in our measurements, because the diffusion layer is *not* affected significantly by a small perturbation during the time the signal is taken, not for the reason Lasia points out. One observes identical results to ours when a rotating disk electrode is used, where the diffusion layer is not affected significantly by small ac waves. We have already pointed out that the Warburg impedance was not observed in our measurements for this reason. That is, we do not deny that the Warburg

(1) Yoo, J.-S.; Park, S.-M. *Anal. Chem.* 2000, 72, 2035.

(2) Spanier, J.; Oldham, K. B. *An Atlas of Functions*; Hemisphere Publishing Corporation: New York, 1987; Chapter 9.

(3) Gabel, R. A.; Roberts, R. A. *Signals and Linear Systems*, 3rd ed.; Wiley: New York, 1987.

(4) Spanier, J.; Oldham, K. B. *An Atlas of Functions*; Hemisphere Publishing Corporation: New York, 1987; Chapter 26.

(5) Gabel, R. A.; Roberts, R. A. *Signals and Linear Systems*, 3rd ed.; Wiley: New York, 1987; pp 266–275.

component cannot be measured by this method. Note, however that this situation is quite different from the differential pulse voltammetry experiment, in which another pulse is given to affect the diffusion layer.<sup>6</sup>

Regarding the comment on the fast relaxation, he (Lasia) is requested to examine eqs 4–7 in our paper, all of which indicate that the current decay is determined by a time constant consisting of  $C_d$  (double layer capacitance) and a parallel resistor composed of  $R_s$  (solution resistance) and  $R_p$  (polarization resistance), not just  $R_p$ . This is not what we electrochemists have been understanding. For this reason, the decay is much faster than expected from the  $R_p$  values alone. However, it should take much longer if the reaction requires a large overpotential because of slow electron-transfer kinetics.

Compare this situation with chronocoulometric experiments, for example, in which similar observations are made.<sup>6</sup> Although the data acquisition time was very short in our system, there must be systems in which the current transient could last much longer, resulting in a Dirac  $\delta$  function with much longer bases for the electrochemical reactions of poor kinetics. As Lasia points out, this technique may not be appropriate for corrosion and intercalation studies, but there is no question that this

technique reduces the time by a few orders of magnitude, even though the Dirac  $\delta$  functions with larger time bases are obtained.

Finally, the noisy data are not something unique to this method, but rather are due to the way we ran our experiments and the equipment we used, which may be improved when our electronics improves. In other words, this point is not relevant to the comments on the method. We are currently improving the electronics by a few different methods, such as implementing analog-to-digital converters of higher bit resolution and using a faster communication bus, which may allow us to use the data in a longer time region until the derivative signal becomes 0.

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(6) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980, Chapter 5.