Predictive Zeta Potential Measurement Method Applicable to Nonaqueous Solvents in High-concentration Dispersion Systems for the System of LiClO4-Propylene Carbonate Solution and…

Suzuki, Yoshimasa
Mizuhata, Minoru

(Citation)
Electrochemistry,90(10):103001

(Issue Date)
2022-07-11

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90009552

Electrochemistry
The Electrochemical Society of Japan

Received: May 4, 2022
Accepted: May 9, 2022
Published online: May 13, 2022
Issued: July 11, 2022

https://doi.org/10.5796/electrochemistry.22-66050
https://doi.org/10.50892/data.electrochemistry.19750639

Article
Electrochemistry, **90(10)**, 103001 (2022)

The 66th special feature
"Novel Aspects and Approaches to Experimental Methods for Electrochemistry"

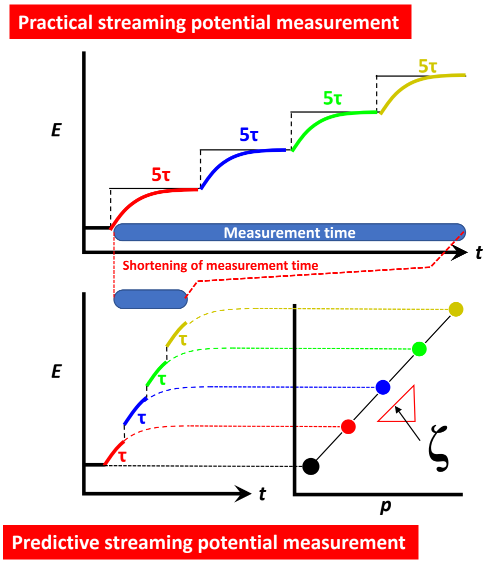
Predictive Zeta Potential Measurement Method Applicable to Nonaqueous Solvents in High-concentration Dispersion Systems for the System of $LiClO_4$–Propylene Carbonate Solution and $LiCoO_2$ Powder Sheet[†]

Yoshimasa SUZUKI[a,§] and **Minoru MIZUHATA**[a,b,*,§§]

[a] *Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe 657-8501, Japan*
[b] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*

* *Corresponding author:* mizuhata@kobe-u.ac.jp

ABSTRACT
We have established a method for measuring the zeta potential generated at the interface between a nonaqueous electrolyte solution utilized in $LiClO_4$/propylene carbonate (PC) electrolyte and lithium cobalt oxide ($LiCoO_2$) by the streaming potential method. Since the surface potential of the metal oxide dispersed in the aprotic nonaqueous solvent contains only a very small amount of water-based potential-determining ions such as H^+ and OH^-, the potential is determined by the adsorption of the solvated electrolyte itself. Unlike aqueous systems with potential-determining ions that exhibit specific adsorption, it took a very long time until the equilibrium state of the ion distribution near the solid surface was reached and the potential stabilized, with a time constant that amounted to about 5 minutes. Therefore, a detailed analysis of the change over time of the potential after the pressure setting showed that the predictive potential showed a change over time with almost a single relaxation having certain time constant. The measurement time of the streaming potential was corresponded to about the time constant, and the resulting zeta potential showed an anomalous concentration dependence as a maximum around 1.0 mol L^{-1} PC and a minimum at 1.5 mol L^{-1} PC for the concentration of each solution.



Keywords : Predictive Zeta Potential, Streaming Potential on Lithium Cobalt Oxide, Nonaqueous Concentrated Electrolyte Solution, Lithium Perchlorate Propylene Carbonate Solution

1. Introduction

It is known that when an electrolytic solution and a solid come into contact with each other, the surface of the solid is charged due to the difference in electrochemical potential between them.[1,2] Since the surface potential generated at the solid-liquid interface changes sensitively reflecting various physical properties of the solid surface and electrolyte composition, it is considered to play an extremely important role in understanding the phenomenon at the solid-liquid interface.[3] The surface potential is evaluated by measuring the zeta potential of the slip surface near the Stern layer of the diffusion layer.[4,5] Electrophoresis is often used to measure the zeta potential of dispersed particles such as oxides,[6,7] polymers,[8,9] metals and their derivatives modified by biomaterials,[10] and so on. This is because the theories related to surface potential are developed with high reliabilities due to physical interpretations assuming various phenomena such as interfacial electrokinetic phenomena,[11] surface heterogeneity of solid phases,[12] relationship between DLVO theory,[13] and application to oxide particles with broad particle size distributions.[14] On the other hand, many common electrochemical materials macroscopically have interface that extends two-dimensionally, such as electrodes and current collectors. The streaming potential method[15,16] and the electroosmotic flow method which can apply any surface potential[17] independent of its planar shape are suitable in their zeta potential measurements.

Recently, increasing research and development of batteries has focused attention on ion transfer at the interface of electrode solid

---

[†] A part of this paper has been presented in the 88th ECSJ Meeting in 2021 (Presentation #1V02).
[§] ECSJ Student Member
[§§] ECSJ Active Member
Y. Suzuki orcid.org/0000-0002-2382-1894
M. Mizuhata orcid.org/0000-0002-4496-2215

materials used for electrode active materials. Nonaqueous electrolyte solutions are the primary electrolytes in the research and development of high-voltage batteries because of their wide potential window. In studying ion transfer and reaction mechanisms at the interface with solids, there has been much discussion concerning the adsorption and orientation of ions and solvents. However, although there have been some calculations based on molecular theory and discussions based on changes in reaction time constants due to impedance response, there have been few discussions on interface chemistry based on classical interface electrokinetic phenomena. Since nonaqueous electrolyte solutions are used and their concentrations are relatively concentrated ($>$ca. $1\,\mathrm{mol\,L^{-1}}$), which are much higher than the concentrations generally used for interfacial electrokinetic phenomena measurements, both measurement and interpretation methods for zeta potential are still in their infancy in such cases.

For the zeta potential measurement in nonaqueous solvents, especially in zeta potential measurement using the streaming potential method, it is difficult to obtain reproducible and reliable numerical values because it fluctuates with time and hysteresis and a constant potential cannot be obtained. Initial zeta potential measurements in nonaqueous systems have been performed along with the development of interfacial chemistry as in the case of aqueous solution systems. In particular, nonaqueous solvents have been the subject of discussions on the potential of the liquid/liquid interface in the emulsification process of paints and oil/water interfaces, as well as on the interfacial potential, and organic solvents with a wide range of relative permittivities have been the target such as the studies by Gortner[18] and Tari[19] etc. In particular, Tari suggests that the electrolytes we are dealing with in our studies of nonaqueous systems are dilute, and that the potential-determining ions are not as clear-cut as in aqueous systems, making it difficult to define their meaning even when zeta potentials are obtained. Kosmulski[20] and Rosenholm[21] summarized that surface potential depends on the number of solvent donors based on zeta potential measurements in the concentration range below $10^{-3}\,\mathrm{mol\,L^{-1}}$. Most of these studies were concerned with the stability of colloidal dispersion systems in nonaqueous solvents for substances that are expected to be used in concentrated dispersion systems with high solid phase fractions, such as pigments used in paints, cosmetics, and other products.[22] Van der Hoeven et al. does not contrast aqueous solvents with nonaqueous solvents, considers them as one of the high dielectric solvents, systematically organizes solvents and dispersants, and summarizes the correlation between zeta potential and dispersion stability.[23] Discussions on the reliability of the measurement method in zeta potential in nonaqueous systems have been made through studies interpreting the state of surface charging from the structure of the electric double layer,[24] comparison with measurements in aqueous systems,[25] and analysis of the electric osmotic flow in capillaries.[26] A surface charge of active materials is an important factor in the electrode fabrication method using electrophoresis method.[27] In such cases, support salts are rarely included, and solvents with relatively low dielectric constants are used to ensure IR drop in the electrolyte. Therefore, the zeta potential in highly concentrated electrolytes has rarely been observed.

In the other utilization, zeta potential in nonaqueous solvents is used to evaluate the dispersibility of fibrous materials such as carbon nanotubes in organic solvents, and the stability and various properties of the surfaces of various electrodes inside batteries.[28]

Because of the relatively high electrolyte concentrations used in batteries, as mentioned above, it is necessary to discuss zeta potential measurement methods for concentrated solutions and their implications. For example, we have studied the conductivity of $LiClO_4$/PC-DME solution impregnated in lithium cobalt oxide ($LiCoO_2$) powder.[29]

The objective of this study is to establish the zeta potential measurement by the predictive method in the vicinity of nonaqueous electrolyte solution using $LiClO_4$/propylene carbonate (PC) and lithium cobalt oxide ($LiCoO_2$) surfaces that do not contain specific adsorption-based potential-determining ions. This method will enable rapid zeta potential measurement at a composite electrode in any concentration range on complicated interfaces with slow ion adsorption and permeation. This method is expected to provide fundamental knowledge of the concentration dependence of zeta potential and the relationship of adsorption and ion solvation structures to the solid phase and ion conduction near the interface.

2. Experimental

2.1 Samples

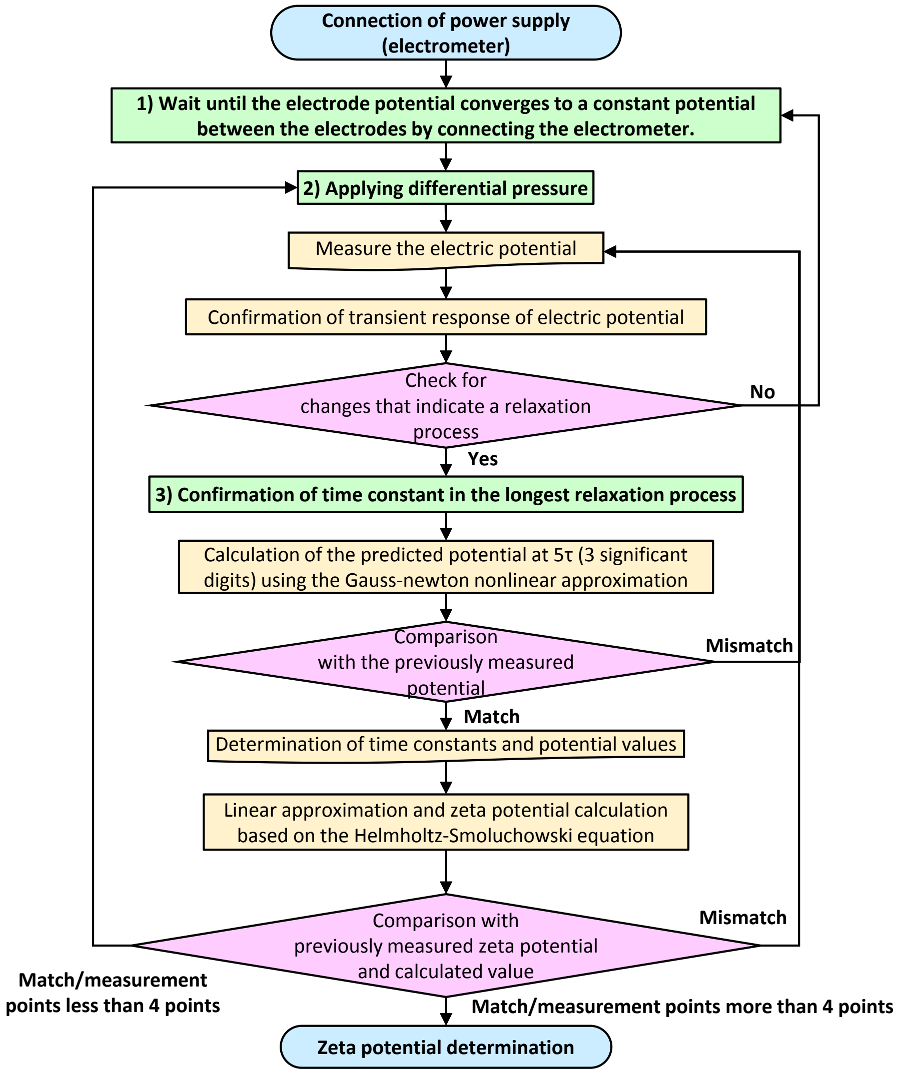
We dehydrated propylene carbonate (PC) (manufactured by Nacalai Tesque Inc.) with Molecular Sieve 4A (manufactured by Nacalai Tesque Inc.) and dried $LiClO_4$ (manufactured by Kishida Chemical Co. Ltd.) at 180 °C for 20 h under vacuum. Then, $LiClO_4$ was dissolved in a PC in a glove box to obtain an electrolytic solution. A dispersion of lithium cobalt oxide ($LiCoO_2$) gifted by Murata Manufacturing Co. Ltd. in *N*-methyl-2-pyrrolidone (NMP) using polyvinylidene fluoride (PVdF) less than 5 wt% as a binder was prepared, coated on the surface of the support, and then dried to prepare a $LiCoO_2$ film for zeta potential measurement.

2.2 Streaming potential measurement

The streaming potential method was chosen as the method for measuring surface potential in concentrated nonaqueous electrolyte solutions. In concentrated solutions, most of the voltage drop applied between the electrodes is concentrated in the electric double layer near the electrodes. The IR drop inside the solution, which is a factor in dispersant migration, is very small, making it difficult to capture particle migration by the electrophoresis method. In addition, battery active materials are often used as coalescing agents together with binders and conductivity aids, and the zeta potential based on the streaming potential with electroosmotic flow is close to the assumption of the actual measurement system to be utilized as a material evaluation method. However, in nonaqueous solvents, there is not always specific adsorption of ions, and the time from the initial measurement to equilibrium tends to be long.[19] Therefore, instead of performing continuous measurement until the streaming potential reaches equilibrium, a method was established to measure the streaming potential by a predictive method. In predicting the change in potential after changing the pressure, we followed the method of predicting exponential potential change with a time constant used in many sensing devices such as predictive thermometers. The zeta potential was calculated according to the algorithm shown in Scheme 1, using three significant digits and an error rate of 20 % as convergence conditions. The main condition for convergence is the value of the streaming potential obtained from the asymptotic value of the exponential function in the determination of the potential at each pressure, and the confirmation of the pressure-potential correlation coefficient in the calculation of the zeta potential obtained from the linear approximation between each pressure value and the streaming potential based on the Helmholtz–Smoluchowski equation. Since the validity of the approximation in the exponential function was confirmed, the zeta potential, ζ, was calculated using the Helmholtz–Smoluchowski equation in the following equation using the steady value V_∞ at each pressure.

$$\zeta = \frac{E}{P}\frac{\eta\lambda}{\varepsilon\varepsilon_0} \tag{1}$$

where E is the streaming potential, P is the pressure, η is the viscosity of the solution, λ is the conductivity of the solution, ε is the



Scheme 1. Algorithm of predictive zeta potential measurement.

relative permittivity, and ε_0 is the permittivity of the vacuum ($8.85 \times 10^{-12}\,\mathrm{F\,m^{-1}}$).

In the practical measurement, the $LiCoO_2$ film was attached to the polypropylene self-made cell shown in Fig. S1 to face each other in parallel using double-sided polypropylene tape. The zeta potential measurement by the streaming potential method was performed with the measuring device shown in Fig. 1. To ensure durability against organic solvents, all tubing and cocks were made of polypropylene or fluoroplastic such as polytetrafluoroethylene (PTFE) or polyperfluoroalkoxyalkane (PFA). In particular, many commercially available streaming potential measuring devices are based on the premise of using an aqueous solution as the flow liquid media, so they use vinyl chloride or butadiene rubber, which have extremely poor chemical resistance, and do not support modification because of the difficulty in ensuring safety against flammable liquids due to the use of organic solvents. It is required to create its own equipment. The use of cellulose filters was also avoided because fouling caused by powdered materials easily occurs in organic solvents.

The electrolytic solution was put into the container and pressurized with dry N_2 whose pressure was adjusted by a regulator to flow the electrolytic solution in the cell. The gap between the $LiCoO_2$ films was adjusted so that the flow rate when pressurized at 700 hPa was about 10–20 $\mathrm{mL\,min^{-1}}$. Platinum wires were installed at both ends of the cell, and the potential difference between both ends was measured using an electrometer TR8652 (ADVANTEST, internal impedance $>10^{13}\,\Omega$). The collection of analog data output from the electrometer was collected as digital data by GRAPHTEC Petit LOGGER. Pressure was monitored by pressure transmitter. After starting the pressurization at 700 hPa, the electrolytic solution continued to flow for a certain period, then the pressurization was stopped, and after standing for a certain period, the pressurization was performed in steps at 100 hPa intervals. In each step, the pressure was maintained for about 2.5–10 minutes, and the change in streaming potential with time was confirmed. After reaching 700 hPa, the pressure was reduced to 0 hPa at intervals of 100 hPa. Furthermore, the change in the streaming potential was confirmed while repeating the cycle of pressurization and depressurization from 0 to 700 and from 700 to 0. The fitting for the calculation of the converged value of the streaming potential, under each pressure, was performed using Kaleidagraph 4.0 (Synergy Software), based on the Levenberg–Marquardt algorithm,[30,31] until the error was less than 20 %. An iterative method was used in the calculation. The fitting results are shown in the same Excel file as the raw streaming potential data D1. The plot of the Helmholtz–Smolokowski equation for each solution used this fitting result.

3. Results and Discussion

Figure S2 shows the temporal change of the streaming potential of the $LiCoO_2$ sheet in a 10 $\mathrm{mmol\,L^{-1}}$ $LiClO_4$ aqueous solution

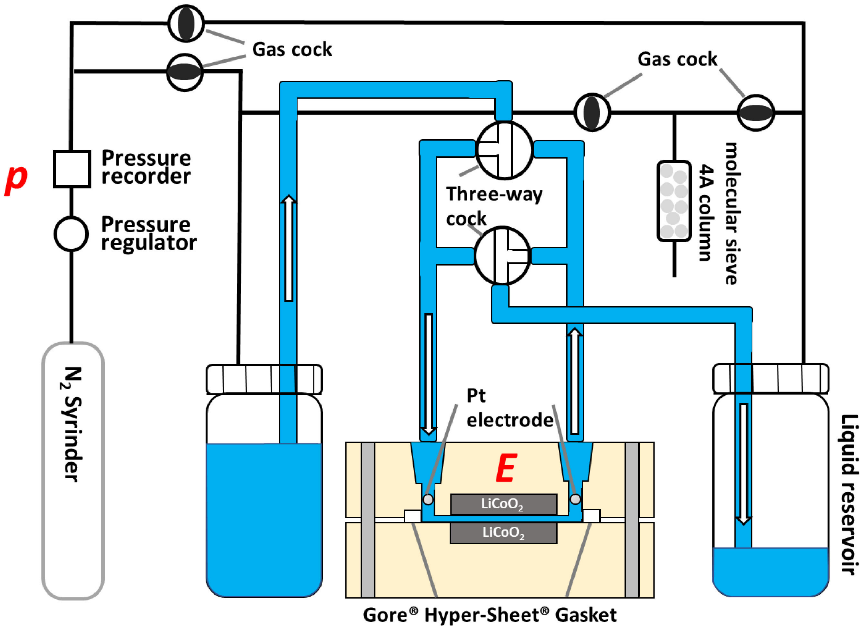


Figure 1. Schematic diagram of streaming potential measuring device.

(pH 5.86). From the start of the measurement to about 160 minutes, the response of the streaming potential to the fluctuation of the external pressure was not reproducible. It is considered that this is because the state inside the cell is not stable. After all, it takes time to impregnate the pores of the $LiCoO_2$ sheet with the electrolytic solution or stabilize the platinum wire. Reproducibility was confirmed in the response of the streaming potential to fluctuations in external pressure exceeding 200 minutes. Furthermore, it was confirmed that the streaming potential showed a transient response when the pressure fluctuated.[32] Hachiya et al. studied the adsorption transient of a potential-determining ion at the solid-liquid interface by the pressure step method in an aqueous solution system.[33] This phenomenon is similar to the response to pressure change in the streaming potential. In the absence of specific adsorbed ions in this system, the potential conversion is slow due to normal ion adsorption, and data acquisition must be waited until the change settles down.

We considered that this transient response included multiple relaxation processes and fluctuated exponentially, and could be expressed by the following equation.

$$-\,\mathrm{d}E(t)/\mathrm{d}t = \Sigma_{\mathrm{i}} C_{\mathrm{i}}/\tau_{\mathrm{i}} \tag{2}$$

$$E(t) = E_\infty + \Sigma_{\mathrm{i}} C_{\mathrm{i}} \exp[-(t - t_0)/\tau_{\mathrm{i}}] \tag{3}$$

Then, first, fitting was performed by the following equation, which is a first-order rate equation including one relaxation process.

$$E(t) = E_\infty + (E_0 - E_\infty)\exp[-(t - t_0)/\tau] \tag{4}$$

Here, $E(t)$ is the streaming potential value at time t, E_∞ is the steady value of the streaming potential at each external pressure, E_0 is the initial value of the streaming potential of each external pressure, τ is the time constant, and t_0 is each initial time at external pressure. Therefore, the steady-state value E_∞ was calculated from the measured values of the streaming potential at each pressure. The result of approximating the numerical value $(E(t) - E_\infty)/(E_0 - E_\infty)$ that standardizes the difference from the initial value E_0 with the exponential function $\exp(-t/\tau)$ by the Gauss–Newton approximation method[34] is shown in Fig. S3a. It was confirmed that the change in the streaming potential measured at each pressure was in good agreement with the approximation formula obtained by the exponential approximation. The time constant τ was about 70 s. From this, we conclude that the fluctuation of the streaming potential includes one relaxation process.

Figure S3a is the result of plotting the relationship between the external pressure and the streaming potential in the part where the 200–700 hPa pressure step was repeated four times. The average value of the zeta potential was −20.5 mV. At 100 hPa, the flow velocity was too low and did not show good agreement with the linear relationship, so it was excluded. Measurements with other aqueous solutions are discussed at supporting information.

Subsequently, the solvent was changed to PC, and the zeta potential was measured with 1.0 mol L^{-1} $LiClO_4$ PC solution. Figure 2 shows the transient response of $(E(t) - E_\infty)/(E_0 - E_\infty)$ when pressurized from 0 to 700 hPa for 1.0 mol L^{-1} $LiClO_4$ aqueous solution and 1.0 mol L^{-1} $LiClO_4$ PC solution. The time constant was calculated because a linear relationship was found in the semi-logarithmic plot, and the time constant was 62.4 s in the water system and 6.15 min in the PC system. It was clarified that the relaxation time of the PC system is about 6 times longer than that of the water system. In order for the value to asymptotically approach equilibrium and to obtain an accuracy of 3 or more significant digits, the measurement time must theoretically be 4.606 times $(1 - \exp(-4.606) < 10^{-3})$ longer than the time constant, and regression calculations must be performed. On the other hand, a regression calculation can be performed for each value obtained, a provisional time constant can be calculated from the value, and once the value of the time constant converges, the converged value of the potential can be calculated as shown in Fig. 2b.

We considered that the cause of such relaxation phenomenon is the relaxation response derived from ion adsorption and diffusion on the surface of the $LiCoO_2$ film or the stress relaxation phenomenon caused by the strain of the electric double layer. First, unlike the water system, there are no ion species that specifically adsorb in the PC system, so it is expected that the time required for ion adsorption will belong. In addition, when interpreted from the mechanical relaxation phenomenon, the Reynolds number of the fluid flowing in the cell is calculated to be about 500, and it is considered that the fluid in the cell in this experiment forms a laminar flow. In this case, it is considered that considerable stress is applied as normal stress to the $LiCoO_2$ sheet installed on the wall surface in the cell. Although the liquid is incompressible, it has been found that the viscosity of

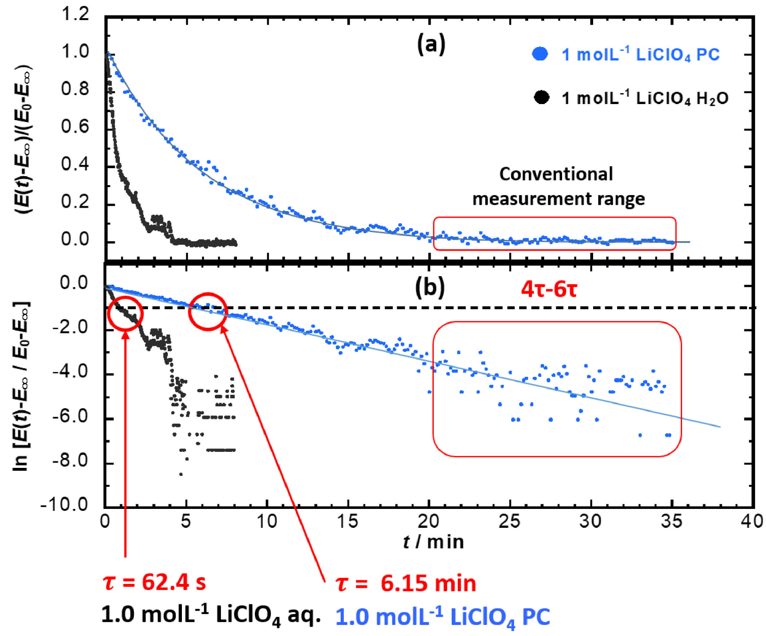


Figure 2. The transient response of (a) $(E(t) - E_\infty)/(E_0 - E_\infty)$ and (b) $\ln[E(t) - E_\infty/E_0 - E_\infty]$ when pressurized from 0 to 700 hPa for 1.0 mol L^{-1} $LiClO_4$ aqueous solution and 1.0 mol L^{-1} $LiClO_4$ PC solution.

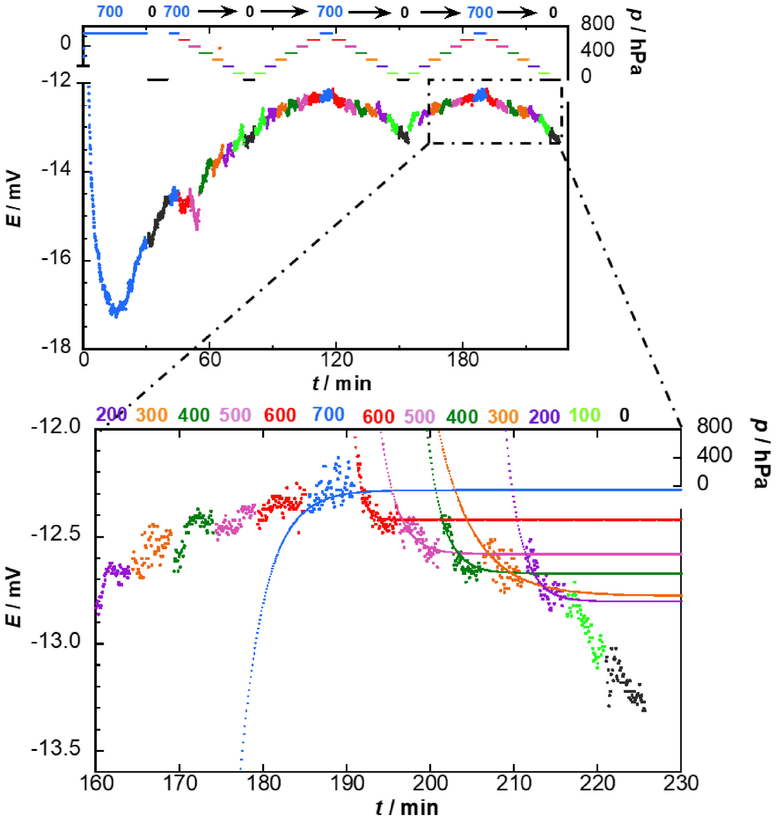


Figure 3. The transient response and results of an exponential approximation for the streaming potential of the $LiCoO_2$ sheet in a 1 mol L^{-1} $LiClO_4$ PC solution at each pressure after 185 minutes.

the solvent increases extremely at the solid-liquid interface when a higher-order structure is formed at the solid-liquid interface due to the bipolar interaction.[35–37] When compressive stress or shear stress is applied to a highly viscous liquid, it is considered to exhibit relaxation behavior in response.[38,39] Since this relaxation behavior is considered to indicate a longer relaxation process in the highly viscous PC system than in the water system, it can be inferred that the relaxation process of the change in the streaming potential took time. As described above, it is considered that the increase in the viscosity of the solution at the solid-liquid interface is the cause of the exponential fluctuation of the streaming potential with the relaxation time peculiar to the measurement sample. Therefore, the relaxation phenomenon of the streaming potential provides a means for directly observing the distortion of the electric double layer model and the state of the relaxation, which have been unknown until now.

Figure 3 shows the temporal change of the streaming potential and an exponential approximation for each pressure after 185

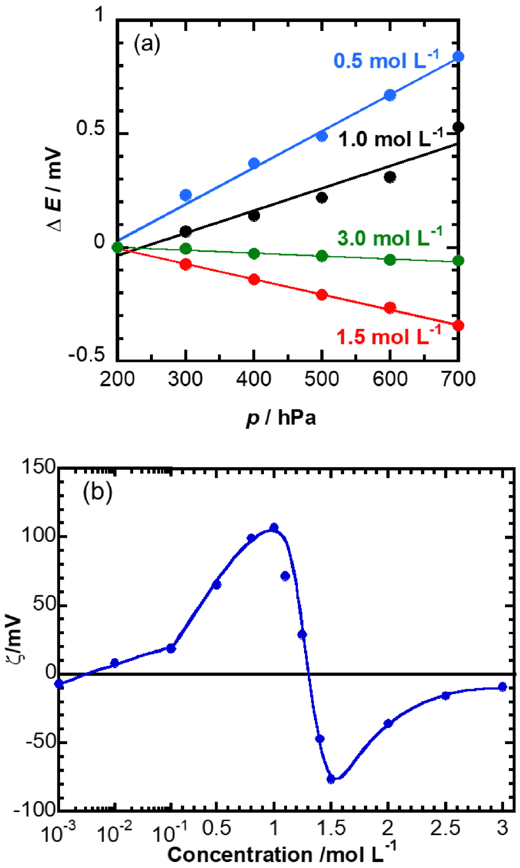


Figure 4. (a) The relationship between the external pressure and the streaming potential by measuring at various $LiClO_4$ concentrations. (b) The concentration dependence of the zeta potential at the interface between the $LiClO_4$ solution and the $LiCoO_2$ sheet.

minutes in a 1.0 mol L^{-1} $LiClO_4$ PC solution of the $LiCoO_2$ sheet in a 1.0 mol L^{-1} $LiClO_4$ PC solution. As in the case of the aqueous solution, an exponential function approximation was performed using Eq. 4 at each pressure step from 80 minutes after the streaming potential showed a response to the external pressure. As shown in imposed figure of Fig. 3, good fitting was confirmed even in the PC system. As shown in Fig. S6, fitting is performed by Eq. 4 even at various concentrations, and the relationship between pressure and the streaming potential is shown in Fig. 4a. A good linear relationship is confirmed regardless of the concentration. Figure 4b shows the concentration dependence of the zeta potential at the interface between the $LiClO_4$ solution and the $LiCoO_2$ sheet calculated using Eq. 1 from these slopes. Raw data for all measurements can be obtained from supporting information. According to the results, the zeta potential increases with increasing concentration, showing a maximum at 1.0 mol L^{-1} and a minimum at 1.5 mol L^{-1}, whereas it became negative in the concentration range suitable for conventional zeta potential measurements (10^{-3}–10^{-1} mol L^{-1}). This change is explained by the adsorption of Li ions in solution and the change in adsorption behavior based on ion pair formation in the high concentration region. In this discussion, the solvation structure of the dissolved species is explained by spectroscopic analysis and ionic conductivity measurements, which will be discussed further in a follow-up study.[40]

4. Conclusions

We have devised a highly reliable measurement method for zeta potential measurement by the streaming potential method in a nonaqueous solvent. From the viscoelastic properties of the solution at the solid-liquid interface, it was clarified that the fluctuation of the streaming potential has a relaxation time peculiar to the measurement sample and fluctuates exponentially. It was confirmed that the relaxation time of the PC system is relatively longer than that of the water system. Therefore, we devised a method to calculate the convergence value of the streaming potential under each pressure by fitting with an exponential function and succeeded in calculating the zeta potential in a nonaqueous solvent. It has also been shown to be useful for the analysis of previously unknown viscoelastic properties of solutions at solid-liquid interfaces. This method provides a means to analyze the various mitigation behaviors of the electric double layer and can contribute to the knowledge for understanding the dynamic state of the electric double layer.

Acknowledgment

Lithium cobalt oxide sheet was gifted by Murata Manufacturing Co. Ltd. The author would like to thanks Mr. Izaya Okae of Murata Manufacturing for fruitful discussion. Y. S. is very grateful to the Next-Generation Outstanding Doctoral Human Development Project through Co-creation in Different Fields in the Support for Pioneering Research Initiated by the Next Generation (SPRING, Grant no. PMJSP2148) of the Japan Science and Technology Agency (JST) for making his study possible by the financial support.

CRediT Authorship Contribution Statement

Yoshimasa Suzuki: Data curation (Lead), Formal analysis (Lead), Methodology (Lead), Validation (Lead), Writing – original draft (Lead)

Minoru Mizuhata: Data curation (Supporting), Formal analysis (Equal), Funding acquisition (Lead), Methodology (Equal), Project administration (Lead), Resources (Lead), Software (Lead), Supervision (Lead), Validation (Lead), Writing – original draft (Supporting), Writing – review & editing (Lead)

Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

Funding

Japan Science and Technology Agency: PMJSP2148

References

D1. Y. Suzuki and M. Mizuhata, *J-STAGE Data*, https://doi.org/10.50892/data.electrochemistry.19750639, (2022).
1. D. L. Chapman, *Philos. Mag.*, **25**, 475 (1913).
2. D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).
3. W. Schmickler, *Chem. Rev.*, **96**, 3177 (1996).
4. P. H. Wiersema, A. L. Loeb, and J. Th. G. Overbeek, *J. Colloid Interface Sci.*, **22**, 78 (1966).
5. R. W. O'Brien and R. J. Hunter, *Can. J. Chem.*, **59**, 1878 (1981).
6. M. Kosmulski, *J. Colloid Interface Sci.*, **337**, 439 (2009).
7. S. Z. Li and R. K. Xu, *Colloids Surf., A*, **326**, 157 (2008).
8. A. Otsuki, *Electrophoresis*, **39**, 690 (2018).
9. R. Hidalgo-Alvarez, J. A. Moleon, F. J. De Las Nieves, and B. H. Bijsterbosch, *J. Colloid Interface Sci.*, **149**, 23 (1992).
10. S. Liu and M. Lämmerhofer, *Electrophoresis*, **40**, 2438 (2019).
11. R. W. O'Brien and L. R. White, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1607 (1978).
12. D. Velegol, J. D. Feick, and L. R. Collins, *J. Colloid Interface Sci.*, **230**, 114 (2000).
13. R. Hidalgo-Álvarez, A. Martín, A. Fernández, D. Bastos, F. Martínez, and F. J. de las Nieves, *Adv. Colloid Interface Sci.*, **67**, 1 (1996).
14. J. W. Ntalikwa, R. Bryant, and J. S. M. Zunzu, *Colloid Polym. Sci.*, **279**, 843 (2001).
15. C. Werner, H. Körber, R. Zimmermann, S. Dukhin, and H. J. Jacobasch, *J. Colloid*

Interface Sci., **208**, 329 (1998).

16. R. J. Yang, L. M. Fu, and C. C. Hwang, *J. Colloid Interface Sci.*, **244**, 173 (2001).
17. P. Saha and I. V. Zenyuk, *J. Electrochem. Soc.*, **168**, 046511 (2021).
18. R. A. Gortner, *Trans. Faraday Soc.*, **35**, 63 (1940).
19. I. Tari, *J. Jpn. Soc. Colour Mater.*, **43**, 510 (1970) [in Japanese].
20. M. Kosmulski, *Colloids Surf., A*, **159**, 277 (1999).
21. J. B. Rosenholm, *Adv. Colloid Interface Sci.*, **259**, 21 (2018).
22. A. Kitahara, *Prog. Org. Coat.*, **2**, 81 (1973).
23. Ph. C. Van Der Hoeven and J. Lyklema, *Adv. Colloid Interface Sci.*, **42**, 205 (1992).
24. A. N. Zhukov, *Adv. Colloid Interface Sci.*, **134–135**, 330 (2007).
25. S. F. Alkafeef and A. F. Alajmi, *Colloids Surf., A*, **289**, 141 (2006).
26. C. Schwer and E. Kenndler, *Anal. Chem.*, **63**, 1801 (1991).
27. K. Ui, S. Funo, H. Nagase, Y. Idemoto, and N. Koura, *Electrochemistry*, **74**, 474 (2006) [in Japanese].
28. P.-C. Ma, N. A. Siddiqui, E. Mäder, and J.-K. Kim, *Compos. Sci. Technol.*, **71**, 1644 (2011).
29. Y. Suzuki, H. Maki, M. Matsui, and M. Mizuhata, *Electrochemistry*, **87**, 294 (2019).
30. K. Levenberg, *Q. Appl. Math.*, **2**, 164 (1944).
31. D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
32. A. Sze, D. Erickson, L. Ren, and D. Li, *J. Colloid Interface Sci.*, **261**, 402 (2003).
33. K. Hachiya, M. Ashida, M. Sasaki, H. Kan, T. Inoue, and T. Yasunaga, *J. Phys. Chem.*, **83**, 1866 (1979).
34. A. Björck, *9. Nonlinear Least Squares Problems*, in *Numerical Methods for Least Squares Problems*, SIAM Publication Library, pp. 339–358 (1996). (https://doi.org/10.1137/1.9781611971484.ch9).
35. M. Mizukami and K. Kurihara, *Chem. Lett.*, **28**, 1005 (1999).
36. M. Mizukami, M. Moteki, and K. Kurihara, *J. Am. Chem. Soc.*, **124**, 12889 (2002).
37. M. Kasuya and K. Kurihara, *Electrochemistry*, **82**, 317 (2014).
38. T. Fujitani, J. Akui, and M. Kawaraya, *J. Jpn. Soc. Colour Mater.*, **67**, 223 (1994). [in Japanese]
39. M. Mizukami and K. Kurihara, *Rev. Sci. Instrum.*, **79**, 113705 (2008).
40. Y. Suzuki, H. Maki, M. Matsui, M. Mizuhata, I. Okae, K. Morizawa, and M. Nagamine, *The 88th Meeting of The Electrochemical Society of Japan*, #1V03 (2021). [in Japanese]