Molecular adsorption at electrolyte/ α - Al_2O_3 interface of aluminum electrolytic capacitor revealed by sum frequency vibrational spectroscopy

Ming Jia,¹ Xiaoyu Hu,¹ Jin Liu,^{1,a)} Yexiang Liu,¹ and Liang Ai^{2,b)}

¹*School of Metallurgy and Environment, Central South University, 932 Lushan South Road, Changsha City 410083, China*

²*The Aihua Group, East Taohualun Road, Yiyang City 413000, China*

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The operating voltage of an aluminum electrolytic capacitor is determined by the breakdown voltage (U_b) of the Al_2O_3 anode. U_b is related to the molecular adsorption at the Al_2O_3 /electrolyte interface. Therefore, we have employed sum-frequency vibrational spectroscopy (SFVS) to study the adsorption states of a simple electrolyte, ethylene glycol (EG) solution with ammonium adipate, on an α - Al_2O_3 surface. In an acidic electrolyte ($\text{pH} < 6$), the Al_2O_3 surface is positively charged. The observed SFVS spectra show that long chain molecules poly ethylene glycol and ethylene glycol adipate adopt a “lying” orientation at the interface. In an alkaline electrolyte ($\text{pH} > 8$), the Al_2O_3 surface is negatively charged and the short chain EG molecules adopt a “tilting” orientation. The U_b results exhibit a much higher value at $\text{pH} < 6$ compared with that at $\text{pH} > 8$. Since the “lying” long chain molecules cover and protect the Al_2O_3 surface, U_b increases with a decrease of pH. These findings provide new insights to study the breakdown mechanisms and to develop new electrolytes for high operating voltage capacitors. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983698>]

I. INTRODUCTION

Aluminum electrolytic capacitors are one of the most widely applied electric components in the electronics industry.^{1–7} With the development of green energy resource applications, such as new energy vehicles, wind power, and LED luminaires, higher circuit efficiency and the ability to withstand current or voltage are required.^{8–11} Under a high operating voltage, the circuit efficiency will be improved. Therefore, high operating voltage aluminum electrolytic capacitors are in demand.

The capacitor operating voltage is one of the crucial factors that determine the performance of capacitors and is influenced by electric breakdown or the destruction of the dielectric Al_2O_3 film on the aluminum anode. Therefore, the voltage at which electric breakdown occurs (breakdown voltage) is directly related to the operating voltage. Hence, the mechanisms of electric breakdown have been widely studied. Many theories describing the behavior of the electric breakdown in a dielectric Al_2O_3 film have been introduced by previous studies.^{12–15} Young suggested that the breakdown may take place at the interface of the oxide and electrolyte.¹⁵ Alwitt attributed the breakdown to the impact of anions from the electrolyte and the flaws in the anodic oxide film being attacked preferentially.^{13,14} Ikonopisov suggested that electrons, originating from anions of electrolytes, were injected to the Al_2O_3 film. When these electrons were accelerated to a certain energy, secondary electrons were released, leading to an avalanche

multiplication from the bulk Al_2O_3 film.¹² Accordingly, electric breakdown occurred. Alwitt and Ikonopisov's theory has been commonly accepted by researchers.^{16–18} Meanwhile, it is agreed that the working electrolyte of capacitors plays a major role in the electrochemical performance of electrolytic capacitors.^{3,5} The electrolyte provides ions that raise the conductivity and decrease the internal resistance, and heals the fissure of anodic oxide films (Al_2O_3) so that the anodic aluminum can be re-anodized to maintain a stable working state, which thus extends the life span of capacitors. Therefore, the electrolyte/ Al_2O_3 interface should be closely related to the breakdown voltage of the Al_2O_3 film.¹⁹

Anodic and cathodic reactions can be described by the following chemical equations:

When the electrode is electrified, the electrolyte will inject OH^- into the alumina surface, and the high field strength will accelerate electrons produced by OH^- to release secondary electrons according to Equations (1) and (2), which will impact the Al_2O_3 film. With cation flow to the cathode, hydrogen is produced. When the voltage reaches a certain value, sparks will occur on the Al_2O_3 surface, suggesting the beginning of the electron avalanche breakdown. Meanwhile, oxygen is observed on the anode foil when electric breakdown occurs.^{13,20–23}

Owing to the absence of a direct interfacial detecting tool to investigate the molecular adsorption states at the interface,

^{a)}E-mail: jinliu@csu.edu.cn

^{b)}E-mail: postdoctor@aihuaglobal.com

the breakdown mechanism remains unclear. Herein, we propose a powerful interface probing tool, sum-frequency vibrational spectroscopy (SFVS), to investigate the behavior of the adsorption of electrolytes on an Al_2O_3 surface. As a second-order nonlinear spectroscopic technique, SFVS has already been applied in probing air/liquid, air/solid, and solid/liquid interfaces.^{24–30} Additionally, SFVS has shown a strong ability to study the orientation, adsorption, and bonding formation of interfacial molecules.^{31–33} Besides, breakdown voltage tests were performed by impregnating the formed anodic foil into the electrolyte. Relationship between the breakdown of an anodic Al_2O_3 film and electrolyte interfacial molecular adsorption states is explored. This may provide new routes to improve the electrochemical performances of electrolytic capacitors.

II. EXPERIMENTAL

A. Materials

A sapphire prism ($\alpha\text{-Al}_2\text{O}_3$) with a crystal orientation (0001) was obtained from Chuanyi Automation Co, Ltd. Capacitor grade ethylene glycol (EG) and ammonium adipate (AA) were purchased from CAPCHEM Technology Co. Ltd, and poly ethylene glycol (PEG) and ethylene glycol adipate (EGA) were produced during the preparation of the electrolytes, of which the molecular structures are shown in Scheme 1.

B. Sample preparation

A sapphire prism was cleaned in a solution of concentrated sulfuric acid for 24 h at 20 °C. Then, it was rinsed by H_2O , ethanol, acetone, and then H_2O (resistivity: 18.2 $\text{M}\Omega\cdot\text{cm}$) in sequence from a Milli-Q purification system and dried by air. A plasma cleaner was used to clean the prism. In addition, a Teflon sample cell was designed to seal the prism/solution for the SFVS measurement. The cell was cleaned in piranha solution for 24 h. The cell was rinsed with H_2O and then assembled with the prism for the SFVS experiments.

Electrolytes with EG as a solvent and AA as a solute were prepared by the following process: 2.5 wt. % AA was added into EG when the temperature of EG was raised to 60 °C, then the solution was kept at approximately 140 °C for 40 min. Long chain molecules, poly ethylene glycol (PEG), and ethylene glycol adipate (EGA) were produced at high temperature, as shown in the following equations:

SCHEME 1. Scheme of ethylene glycol (EG), ammonium adipate (AA), poly ethylene glycol (PEG), and ethylene glycol adipate (EGA).

Boric acid and ammonia water were used to regulate the pH values of the electrolyte. The breakdown voltage and pH value were measured by a T-V tester (DAGONG Electronic) and pH meter (Shanghai Instrument Electric Science Instrument Co, Ltd), respectively. A TV-1000B tester was used to test the breakdown voltage of the formed aluminum foil impregnated into the electrolytes. Aluminum foils were applied as both anode and cathode. The constant current mode was set with 20 mA current intensity. The voltage in this system was continuously increased and tended to be stable. The value of the breakdown voltage was collected from the voltage in the stable stage.

C. SFVS and FTIR experiments

The SFVS system was a commercial sum-frequency generation spectrometer from EKSPLA Ltd. The detailed setup has been reported previously.^{34,35} Briefly, a Nd:YAG laser produced visible light at 532 nm and the optical parametric generator/amplifier (OPG/OPA) generated a tunable IR beam (from 4000 to 1000 cm^{-1}). The visible beam with $\sim 4.5 \mu\text{J}/\text{pulse}$ and IR beam with $\sim 3.5 \mu\text{J}/\text{pulse}$ were overlapped spatially and temporally at the $\alpha\text{-Al}_2\text{O}_3$ prism/electrolyte interface to produce an SFVS signal, both having a pulse width of ~ 30 ps. The incident angles versus the surface normal of the IR and visible beams were about 55° and 60°, respectively. SFVS spectra were collected at 5 cm^{-1} interval. Each point is the average of 200 shots. The region of tunable IR for our experiment was applied from 2700 to 3900 cm^{-1} . The polarization combination was SSP (S for SFVS, S for visible, and P for IR). The SFVS spectra were normalized by the laser power of the IR beam. FTIR measurements were applied by Thermo Nicolet iS5 FT-IR to analyze various moieties from the electrolytes.

D. Design of a spectra-electrochemical Teflon cell

A self-designed Teflon cell was prepared for the sapphire prism ($\alpha\text{-Al}_2\text{O}_3$)/electrolyte interface. Fig. 1 shows the structure of the cell. The cleaned semi-cylinder prism was compressed on top of the cell and fixed by a designed locker with screws. The electrolyte was injected into the liquid

FIG. 1. Photo and scheme for the SFVS sample cell.

chamber through the front tunnel using a syringe, with outflow through the tunnel on the right. The outflow tunnel was connected with a thin hose. When the chamber was filled with the electrolyte, a liquid/solid interface was created for the SFVS experiment.

III. RESULTS AND DISCUSSION

A. Breakdown voltage examination

The breakdown voltage of the aluminum foil in the electrolytes at different pH values was measured. As Fig. 2 shows, the breakdown voltage exhibits a negative correlation with pH values. From pH = 3.75 to 5.96 and 8.08 to 10.08, decreases in U_b of approximately 10 V were observed. However, when the pH of the electrolyte changed from acidic (5.96) to alkaline (8.08), it was interesting to see that U_b significantly dropped from 546 to 510 V. U_b was reduced by more than 35 V. The difference in U_b variation with pH might be caused by the different adsorption states of the molecules at the electrolyte/ Al_2O_3 interface.

B. SFVS spectra of the electrolyte/ Al_2O_3 interface and FTIR spectra of the electrolyte at different pH values

In order to obtain interfacial molecular information at different pH, SFVS was used to investigate the electrolyte/ Al_2O_3 interface as shown in Fig. 3. A sapphire prism, $\alpha\text{-Al}_2\text{O}_3$, was used to simulate the Al_2O_3 film of the anode foil electrode used in the breakdown voltage test. The peaks at 2850 cm^{-1} and 2950 cm^{-1} are from the CH_2 symmetric stretching ($\text{CH}_2\text{-SS}$) and CH_2 asymmetric stretching ($\text{CH}_2\text{-AS}$), respectively.^{36–38} There is a remarkable difference of CH_2 peaks between acidic and alkaline electrolytes. This suggests that the adsorption

FIG. 2. Breakdown voltage as a function of pH values.

states of the interfacial electrolyte molecules are different. Additionally, the strong and noisy signal in the SFVS spectra at $3600\text{--}3900\text{ cm}^{-1}$ is possibly assigned to the $(\text{Al})_2\text{OH}$ groups on the Al_2O_3 surface, which is in agreement with the report.³⁹ This peak is intense, most likely not because the peak is so strong, but due to the enhancement of the Fresnel factors at the high frequency side.⁴⁰ According to the previous research at $\text{Al}_2\text{O}_3/\text{metal}/\text{water}$ and $\text{Al}_2\text{O}_3/\text{metal-oxide}/\text{water}$ interfaces, the Fresnel factors were strongly dependent on the frequency of the IR beam that nearly dominated the signal of the SFVS spectra.⁴¹ In addition, the water vapor in the air may absorb the IR intensity between 3600 and 3900 cm^{-1} that may affect (possibly decrease) the SFVS intensity and result in the noisy signal. Hence, this wide and noisy peak is a comprehensive result.

The influence of AA on the molecular adsorption at the interface was investigated by changing the AA content and the corresponding SFVS spectra were recorded. As Fig. 4 shows, at pH ~ 6 the electrolytes with 0.5 wt. %, 2.5 wt. %, and

FIG. 3. SFVS SSP spectra of electrolytes with different pH values at the Al_2O_3 interface. The AA weight percentage in the electrolyte is 2.5%.

FIG. 4. SFVS SSP spectra of electrolytes with 0.5%, 2.5%, and 5.0% weight percentage of AA in the electrolyte at pH ~ 6 and pH ~ 9.

5.0 wt. % presented a weak CH₂-SS peak, while at pH ~ 9 the peak became strong.

Since PEG and EGA were produced during the boiling process of electrolyte preparation, molecules in the electrolyte

would be PEG, EGA, EG, AA, and H₂O (H₂O tested to be ~1 wt. %). The following protonation/deprotonation processes are expected in the electrolytes over the experimental pH range from 3.75 to 10.08:^{42,43}

The point of zero charge (pzc) of $\alpha\text{-Al}_2\text{O}_3$ (0001) appears at pH ~ 6.3 for the water/ $\alpha\text{-Al}_2\text{O}_3$ interface. When the bulk liquid presents a pH < 6.3, the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface will gradually be positively charged. On the contrary, the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface will be negatively charged when pH > 6.3.³⁹

When pH < 6 (pH = 3.75, 4.55, and 5.96), EG, PEG, and EGA will barely ionize and some AA anions ($[\text{-COO}^-]/[\text{-COOH}] = 0.06, 0.35, 9.1$) will be present in the electrolyte according to pK in Eqs. (6)–(8). The Al_2O_3 surface possesses positive charges. Weak CH₂-SS and CH₂-AS peaks were detected in the SFVS spectra in an acidic condition.

It is known that in an SFVS spectrum, cancellation of the CH₂ transition dipoles will occur for an all-trans or inversion symmetry conformation.^{26,27} An increase in the asymmetry, such as gauche defects, will result in an increase in the intensity of the CH₂-SS. Hence, there are three scenarios to explain the low CH₂-SS intensity at the interface at pH < 6. (i) A few anions are absorbed on the Al_2O_3 surface. (ii) Interfacial molecules or anions show a “standing” orientation with all-trans conformation. (iii) PEG and EGA molecules prefer to be absorbed at the interface with a “lying” orientation.

In the first scenario, the weak CH₂-SS peaks indicate that a very small amount of AA anions are absorbed on the positively charged surface. In the second scenario, only those negatively charged AA anions with all-trans conformation can lead to the low CH₂-SS intensity. However, the concentration of AA anions is not enough to form an ordered arrangement with the all-trans conformation. In the third scenario, long chain molecules of PEG and EGA will be bonded to the positively charged surface by their O (from -O- and -COO- functional groups) with lone pairs. Once the molecules are bonded to the surface by O, the rest of the O in PEG and EGA will also be bonded and present a “lying” orientation. Therefore, alkyl chains of PEG and EGA molecules show a “lying” orientation on the surface, resulting in a cancellation of the CH₂ transition dipoles.

Under an alkaline condition (pH = 7.11, 8.08, and 10.08), the Al_2O_3 surface is negatively charged. According to Eq. (6), the electrolyte mainly contains AA anions. AA anions will not be attracted to the negatively charged surface because of the electrostatic force at high pH. According to Eqs. (7) and (8), EG and PEG are in molecular states. The molecules can only

be absorbed on the Al_2O_3 surface by hydrogen binding through the terminal OH groups. However, the hydrogen bond is too weak to support the long chain PEG molecules absorbed on the Al_2O_3 surface. Therefore, only the short chain EG molecules will be absorbed on the surface. The SFVS intensity of the CH_2 -SS peak increases rapidly as the pH increases, indicating the adsorbed EG molecules present a disordered arrangement with gauche defects. This means the EG presenting a “tilting” conformation on the Al_2O_3 surface.

FTIR measurements were performed to investigate the molecular structure of bulk electrolytes at different pH. Fig. 5 shows the FTIR spectra of the electrolytes in the acidic (pH 5.96) and alkaline (pH 10.08) solutions. Obviously, the two FTIR spectra were identical, suggesting that the bulk molecular structures were barely changed. The peaks at 2875 cm^{-1} and 2940 cm^{-1} were attributed to CH_2 -SS and CH_2 -AS, respectively. The broad peak centered at 3300 cm^{-1} can be ascribed to OH groups from water, EG, PEG, and EGA. The broad peak at $3000\text{--}3400\text{ cm}^{-1}$ in the FTIR spectra is not observed in the SFVS spectra, while the peak at high frequency range ($3600\text{--}3900\text{ cm}^{-1}$) in the SFVS spectra was not detected in the FTIR spectra. These strongly indicate that the SFVS spectra present the interfacial information of the electrolyte/ Al_2O_3 interface.

C. Mechanism of Al_2O_3 breakdown in electrolytes at different pH values

According to the analysis above, the schemes of molecular adsorption states at the electrolyte/ Al_2O_3 interface are shown in Fig. 6. The possible breakdown mechanism at the electrolyte/ Al_2O_3 interface will be stated according to the molecular adsorption and the results of the breakdown voltage test. In Fig. 6(a), the Al_2O_3 surface is positively charged at $\text{pH} < 6$, as mentioned above. As the breakdown voltage presents a higher value at low pH, the possible scenarios (i) and (iii) can be verified. For scenario (iii), long chain molecules PEG and EGA will be connected to the Al_2O_3 surface with their $-\text{O}-$ and $-\text{COO}-$ functional groups and cover the surface. As a result, the endurance of the Al_2O_3 film is greatly improved and the higher U_b values are detected. However, scenario (i) could not explain the improvement for the breakdown voltage. If the interfacial molecules are unable to cover the surface well, the breakdown voltage should be reduced. Therefore, we

FIG. 5. FTIR spectra of electrolytes at pH 5.96 and 10.08.

FIG. 6. Scheme of molecular conformation at the electrolyte/ Al_2O_3 interface when (a) $\text{pH} < 6$ and (b) $\text{pH} > 8$. The alumina crystal is colored gray. For interfacial molecules, oxygen atoms are colored red, carbon atoms dark gray, and hydrogen atoms white.

conclude that the “lying” adsorption states of long chain molecules lead to a higher breakdown voltage at low pH.

In contrast, the Al_2O_3 surface is negatively charged at $\text{pH} > 8$ as Fig. 6(b) shows. In these conditions, the short chain EG molecules will be adsorbed on the Al_2O_3 surface, presenting disorderly “tilting” states. Owing to the disorder adsorption of short chain EG and its “tilting” states, the Al_2O_3 surface shows relatively less coverage and more gaps are exposed to the electrolyte. In this case, the surface will not be protected as well as under the acidic condition. Hence, with the corrosion of the electrolyte, the endurance of the Al_2O_3 film becomes weaker and the breakdown voltage decreases.

IV. CONCLUSIONS

As an interface sensitive tool, SFVS was applied to study the electrolyte/ Al_2O_3 interface. The relationship between the molecular adsorption states of the electrolyte and the breakdown voltage of the aluminum electrolytic capacitor has been investigated for the first time. The breakdown voltage test shows that U_b of the anode foil drops with increasing electrolyte pH. The SFVS spectra of the electrolyte/ Al_2O_3 interface show that molecular adsorption at the interface is directly influenced by the pH values. According to the results, it is suggested that the electrolyte of an aluminum electrolytic capacitor should be kept under acidic conditions so as to protect the Al_2O_3 surface of the anode foil. New solutes or solvents with long chain molecules can be introduced to the electrolyte to increase the operating voltage for capacitors.

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- ¹M. Ue, M. Takeda, Y. Suzuki, and S. Mori, *J. Power Sources* **60**, 185 (1996).
- ²M. Tsai, Y. Lu, and J. Do, *J. Power Sources* **112**, 643 (2002).
- ³F. Trombetta, R. F. de Souza, M. O. de Souza, and E. M. A. Martini, *J. Appl. Electrochem.* **39**, 2315 (2009).
- ⁴R. Kötz and M. Carlen, *Electrochim. Acta* **45**, 2483 (2000).
- ⁵F. Trombetta, R. F. de Souza, M. O. de Souza, C. B. Borges, N. F. Panno, and E. M. A. Martini, *Corros. Sci.* **53**, 51 (2011).
- ⁶A. Berduque, Z. Dou, and R. Xu, in CARTS-Europe Virtual Conference, 2009.
- ⁷K. Sheng, Y. Sun, C. Li, W. Yuan, and G. Shi, *Sci. Rep.* **2**, 247 (2011).
- ⁸B. Sun, X. Fan, C. A. Yuan, and C. Qian, in International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystems, 2015.
- ⁹J. Both, *IEEE Electr. Insul. Mag.* **31**, 24 (2015).
- ¹⁰K. Zhao, P. Ciufo, and S. Perera, in International Conference on Harmonics and Quality of Power, 2010.
- ¹¹A. M. R. Amaral and A. J. M. Cardoso, *IEEE Trans. Instrum. Meas.* **59**, 1258 (2010).
- ¹²S. Ikonopisov, *Electrochim. Acta* **22**, 1077 (1977).
- ¹³R. S. Alwitt and R. G. Hills, *J. Electrochem. Soc.* **112**, 974 (1965).
- ¹⁴R. S. Alwitt and R. Hills, *IEEE Trans. Parts, Mater. Packag.* **1**, 28 (1965).
- ¹⁵L. Young, *Anodic Oxide Films* (Academic Press, London, New York, 1962).
- ¹⁶S. Petkova, C. Girginov, and T. Petkov, *Adv. Nat. Sci., Theory Appl.* **2**, 23 (2013).
- ¹⁷V. Kadary and N. Klein, *J. Electrochem. Soc.* **127**, 139 (1980).
- ¹⁸T. H. Distefano and M. Shatzkes, *Appl. Phys. Lett.* **25**, 685 (1975).
- ¹⁹M. Winter and R. J. Brodd, *Chem. Rev.* **104**, 4245 (2004).
- ²⁰J. Vitt and D. Johnson, *J. Electrochem. Soc.* **139**, 774 (1992).
- ²¹Y. Li, H. Shimada, M. Sakairi, K. Shigyo, H. Takahashi, and M. Seo, *J. Electrochem. Soc.* **144**, 866 (1997).
- ²²A. Despić and V. P. Parkhutik, *Modern Aspects of Electrochemistry No. 20* (Springer, 1989), p. 401.
- ²³Q. Zhu, Y. Song, X. Zhu, and X. Wang, *J. Electroanal. Chem.* **601**, 229 (2007).
- ²⁴Y. R. Shen and V. Ostroverkhov, *Chem. Rev.* **106**, 1140 (2006).
- ²⁵G. Richmond, *Chem. Rev.* **102**, 2693 (2002).
- ²⁶J. Liu and J. C. Conboy, *Langmuir* **21**, 9091 (2005).
- ²⁷X. Wang, J. Liu, H. Du, and J. D. Miller, *Langmuir* **26**, 3407 (2010).
- ²⁸G. Gonella, C. Lütgebaucks, A. G. F. de Beer, and S. Roke, *J. Phys. Chem. C* **120**, 9165 (2016).
- ²⁹B. Bozzini, B. Busson, C. Humbert, C. Mele, and A. Tadjeddine, *Electrochim. Acta* **218**, 208 (2016).
- ³⁰H. Noguchi, T. Okada, and K. Uosaki, *Electrochim. Acta* **53**, 6841 (2008).
- ³¹A. Opdahl and G. A. Somorjai, *Langmuir* **18**, 9409 (2002).
- ³²H. Chen, G. Wei, B. H. Wu, D. Wu, Z. Zhang, and H. F. Wang, *Chem. Phys. Lett.* **408**, 284 (2005).
- ³³J. Kim and P. S. Cremer, *J. Am. Chem. Soc.* **122**, 12371 (2000).
- ³⁴T. M. Uehara, V. S. Marangoni, N. Pasquale, P. B. Miranda, K. B. Lee, and V. Zucolotto, *ACS Appl. Mater. Interfaces* **5**, 13063 (2013).
- ³⁵X. Zhang, C. Zhang, J. M. Hankett, and Z. Chen, *Langmuir* **29**, 4008 (2013).
- ³⁶M. Zolk, F. Eisert, J. Pipper, S. Herrwerth, W. Eck, M. Buck, and M. Grunze, *Langmuir* **16**, 5849 (2000).
- ³⁷E. L. Hommel, J. K. Merle, M. Gang, C. M. Hadad, and H. C. Allen, *J. Phys. Chem. B* **109**, 811 (2005).
- ³⁸L. Dingfang, M. A. Gang, X. Man, and H. C. Allen, *Environ. Sci. Technol.* **39**, 206 (2004).
- ³⁹L. Zhang, C. Tian, G. A. Waychunas, and Y. R. Shen, *J. Am. Chem. Soc.* **130**, 7686 (2008).
- ⁴⁰J. F. D. Liljeblad, I. Furo, and E. C. Tyrode, *Phys. Chem. Chem. Phys.* **19**, 305 (2017).
- ⁴¹E. H. G. Backus, N. Garciaaraz, M. Bonn, and H. J. Bakker, *J. Phys. Chem. C* **116**, 23351 (2012).
- ⁴²J. B. W. Frandsen, S. Kiil, and J. E. Johnsson, *Chem. Eng. Sci.* **56**, 3275 (2001).
- ⁴³K. K. Kundu, and M. N. Das, *J. Chem. Eng. Data* **9**, 82 (1964).