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A pH Measurement System Suitable for Quaternary Ammonium Carboxylate/ γ -Butyrolactone Electrolytes

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Received August 8, 1996 ; Accepted October 21, 1996

1 INTRODUCTION

Potentiometry in nonaqueous solutions employing ion-selective electrodes^{1,2)} has become an important technique to characterize organic electrolytes for electrochemical devices such as lithium batteries³⁻⁵⁾, electrical double-layer capacitors^{4,6,7)} and aluminum electrolytic capacitors⁸⁻¹²⁾.

Coetzee *et al.* have reported the characterization of reactive impurities in propylene carbonate (PC) and γ -butyrolactone (GBL)¹³⁾. Izutsu *et al.* have studied the acid-base equilibria in those solvents by a conventional glass electrode and Si_3N_4 - and Ta_2O_5 -ISFETs (ion selective field effect transistor)¹⁴⁻¹⁶⁾.

pH measurement has been a conventional and essential quality control technique of ethylene glycol (EG)-based electrolytes for aluminum electrolytic capacitors, because their aluminum oxide dielectrics are most compatible with electrolytes having a weakly acidic pH. Since ethylene glycol solutions have a similar acidity potential range with aqueous solutions¹⁷⁾, an ordinary pH measurement system for aqueous solutions has been applied without any problems.

However, the popularization of quaternary ammonium carboxylate/GBL electrolytes has often caused misunderstanding of pH, because GBL as an aprotic solvent has much wider acidity potential range than amphiprotic solvents and its electrolytes give high pH values beyond expectation.

In this paper, we will present reference and indicator electrodes, which are appropriate for pH measurement of quaternary ammonium carboxylate/GBL electrolytes. Quality control of the GBL-based electrolytes can be well performed by this technique.

2 EXPERIMENTAL

Reagents.— GBL (Mitsubishi Chemical Corp., Battery grade), I_2 , NaI, AgClO_4 and $\text{CF}_3\text{SO}_3\text{H}$ (Wako Pure Chemical Industries, Ltd.) were used without further purification. Et_4NI , Et_4NClO_4 , picric acid (HPic) and phthalic acid (H_2PA) (Wako Pure Chemical Industries, Ltd.) were purified by recrystallization from ethanol, acetone, toluene and water, respectively.

Et_4NPic was prepared by the neutralization of HPic in ethanol with Et_4NOH aqueous solution (SACHEM, Inc., Ultrapure grade) followed by recrystallization from water-ethanol. Et_4NHPA and $(\text{Et}_4\text{N})_2\text{PA}$ were synthesized by the reaction between H_2PA and Et_4NOH followed by recrystallization from acetone.

Water in all 1 mol dm^{-3} (M) GBL solutions was removed below 100 ppm by vacuum evaporation at 50°C while the solvent was refluxed, and their concentrations were calibrated from the weight change.

Cell Assembly.— A double-junction reference electrode¹⁸⁾ with glass frits, a glass electrode, an IrO_2 electrode¹⁹⁾ and a thermocouple (all from Toa Electronics, Order-made) were fixed in a 100 ml glass bottle with a silicone lid as shown in Fig. 1.

In the reference electrode, Pt and Ag wires were used as a contact to an inner solution, and the inner and outer solutions were renewed before every measurement.

Apparatus.— The water content in GBL solutions was measured by a moisture meter (Mitsubishi Chemical Corp., CA-06). Cyclic voltammetry and galvanostatic polarization were carried out by an automatic polarization system (Hokuto Denko Co., HZ-1A), where the same wires with different lengths were used as a working electrode (0.5 ϕ x 20 l) and a counter electrode (0.5 ϕ x 100 l). Potentiometric measurement was carried out by a pH meter (Toa Electronics, HM-11P), whose outputs were monitored by an intelligent recorder (Toa Electronics, INR-6061). All potentiometric titrations were performed in an argon glove box (Eicoh Shokai Co., VDB-CB-6311Y) equipped with a moisture removing apparatus (Vacuum

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Key Words: pH measurement system, γ -Butyrolactone, Quaternary ammonium carboxylates, Aluminum electrolytic capacitors

Atmosphere Co., HE-493) at $30 \pm 1^\circ\text{C}$, and the water content in the cell was kept less than 300 ppm during the titration.

Fig. 1 Cell assembly for potentiometric titration.

3 RESULTS AND DISCUSSION

Among quaternary ammonium carboxylate/GBL electrolytes, tetraalkylammonium hydrogen phthalate solution is mostly used in aluminum electrolytic capacitors due to its excellent thermal stability¹²⁾. Therefore, we have looked for appropriate reference and indicator electrodes for this electrolyte.

Selection of Reference Electrode.— Coetzee *et al.* have recommended to use a $\text{Pt}/(\text{I}_3^- + \text{I}^-)$ reference electrode²⁰⁾ and it was successfully used in many aprotic solvents such as GBL^{10,13)}, PC^{13,20)}, AN²⁰⁾, DMSO²¹⁾, THF²²⁾ and 1,3-dioxolane (DOL)²³⁾. On the other hand, Izutsu *et al.* used a popular Ag/Ag^+ redox couple in GBL^{15,16)} and PC^{14,15)} and other solvents (AN, DMSO, DMF, NMP)¹⁵⁾.

To examine their reversibilities in GBL, exchange current densities i_0 were evaluated directly from the linear sections ($-6 \text{ mV} < \eta < 6 \text{ mV}$) of their cyclic voltamograms in Fig. 2 by means of the following equation²⁰⁾:

$$i_0 = (RT/F)(i/\eta) \quad [1]$$

where R , T , F , i and η are the gas constant, absolute temperature, the Faraday constant, current density and overpotential, respectively. The results are listed in Table 1. Both $\text{Pt}/(\text{I}_3^- + \text{I}^-)$ and Ag/Ag^+ couples showed higher exchange current densities than those reported for PC. Replacement of NaI with Et_4NI increased the exchange current density, however, relatively high electrolyte concentration was required.

After galvanostatic polarization, the $\text{Pt}/(\text{I}_3^- + \text{I}^-)$ electrode returned to its equilibrium potential E_0 quickly

compared with the Ag/Ag^+ couple, which showed a hysteresis as shown in Fig. 3.

Several single-junction electrodes consisting of $\text{Pt}/(50 \text{ mM I}_2 + 100 \text{ mM Et}_4\text{NI in GBL})$ were dipped in the $1 \text{ M Et}_4\text{NHPA/GBL}$ solution, and the potential differences among the two electrodes were measured. The potential differences were within $\pm 1 \text{ mV}$ with reproducibility and the potential difference between a fresh electrode and the one after 1 day was only 2 mV .

On the other hand, single-junction electrodes consisting of $\text{Ag}/(20 \text{ mM AgClO}_4 \text{ in GBL})$ showed potential fluctuations of more than 100 mV after 2 hours due to the clogging of the junction by silver phthalate precipitation. This prevented us from using the Ag/Ag^+

Fig. 2 Plots of current density as a function of overpotential at 25°C and a scan rate of 0.1 mV s^{-1} .

- a) $\text{Pt}/(50 \text{ mM I}_2 + 100 \text{ mM Et}_4\text{NI in GBL})$
- b) $\text{Pt}/(50 \text{ mM I}_2 + 100 \text{ mM NaI in GBL})$
- c) $\text{Ag}/(20 \text{ mM AgClO}_4 \text{ in GBL})$

Table 1 Exchange current densities for I_3^- , I^- and Ag/Ag^+ couples in GBL and PC for reference.

Solv.	Electrolyte	Electrode	$i_0 / \text{A cm}^{-2}$
GBL	10 mM I_2 + 20 mM NaI	Pt	1.2×10^{-5}
	50 mM I_2 + 100 mM NaI	Pt	1.6×10^{-4}
	10 mM I_2 + 20 mM Et_4NI	Pt	5.6×10^{-5}
	50 mM I_2 + 100 mM Et_4NI	Pt	2.7×10^{-4}
	20 mM AgClO_4	Ag	2.0×10^{-4}
PC	50 mM I_2 + 100 mM NaI	Pt	9.0×10^{-5} ¹⁸⁾
	20 mM AgClO_4	Ag	2.0×10^{-5} ²⁴⁾

couple for the "month-long" monitoring, even a bridge salt solution was used.

Effect of water content in the electrolyte on the equilibrium potential of $\text{Pt}/(\text{I}_3^-/\text{I}^-)$ was also examined. Since the equilibrium potential shifted to a positive direction as shown in Fig. 4, a double-junction electrode with a bridge salt solution is recommended for the "day-long" titration to avoid water contamination from an analyte.

Fig. 3 Galvanostatic polarization curves at 25°C.

- a) $\text{Pt} / (50 \text{ mM } \text{I}_2 + 100 \text{ mM } \text{Et}_4\text{NI} \text{ in GBL})$
 c) $\text{Ag} / (20 \text{ mM } \text{AgClO}_4 \text{ in GBL})$

Fig. 4 Effect of water on the equilibrium potential of $\text{Pt} / (50 \text{ mM } \text{I}_2 + 100 \text{ mM } \text{Et}_4\text{NI} \text{ in GBL})$.

Selection of Indicator Electrode.— We have tested a glass electrode and an IrO_2 electrode in GBL. As shown in Fig. 5, the IrO_2 electrode showed faster response than the glass electrode and the difference of equilibrium potentials between these two electrodes was almost constant during a short time titration. However, the equilibrium potential of the IrO_2 electrode in a buffer solution containing an equimolar mixture of HPic and Et_4NPic in GBL¹⁵⁾ changed day by day and shifted 72 mV in a month. Therefore, the IrO_2 electrode should be used with careful calibration before every titration.

Calibration of the System.— 50 ml of $5 \times 10^{-3} \text{ M}$ GBL solutions of Et_4NPic , H_2PA and $(\text{Et}_4\text{N})_2\text{PA}$ were titrated with 1 M GBL solutions of HPic, Et_4NHPA and Et_4NHPA , respectively. The emf of the following cell was plotted as a function of $\log (\text{Ca}/\text{Cs})$ in Fig. 6, where Ca and Cs are the concentrations of an acid and its salt, respectively.

Glass electrode | $\text{Ca HX} + \text{Cs Et}_4\text{NX}$ (GBL)

|| 50 mM Et_4NClO_4 (GBL) ||

50 mM $\text{I}_2 + 100 \text{ mM } \text{Et}_4\text{NI}$ (GBL) | Pt [2]

The glass electrode appeared to give a Nernstian response for HPic/Pic^- (slope = 60.5) and $\text{H}_2\text{PA}/\text{HPA}^-$ (slope = 52.3), however, the potentials of $\text{HPA}^-/\text{PA}^{2-}$ seemed to reach the upper limit in GBL system due to the formation of a ring-opening product (Et_4NGBL) by the reaction between GBL and $\text{PA}(\text{Et}_4\text{N})_2$ as a strong base:

Fig. 5 Potential responses of glass and IrO_2 electrodes during the titration of GBL with $\text{CF}_3\text{SO}_3\text{H}$.

pH^* in Fig. 6 was scaled using $pK_a = 8.35$ for $HPic^{16)}$ and we obtained $pK_a = 12.5$ for H_2PA , which is almost the same as a reported value (12.4)¹⁶⁾.

Titration of GBL.— GBL was titrated with 1 M GBL solutions of CF_3SO_3H , H_2PA , Et_4NHPA , $(Et_4N)_2PA$ and

Et_4NGBL , and emfs were plotted as a function of the logarithmic concentration C in Fig. 7. From these results, the accessible potential range of GBL proved to be about 26 pH scale in our proposed system, which is 3 ~ 4 pH scale smaller than the autoprotolysis constant of GBL¹⁶⁾.

Fig. 6 Glass electrode potentials vs. $Pt(I_3^-+I^-)$ reference electrode in GBL buffer solutions.

Fig. 7 Titration curves in GBL using glass electrode and $Pt(I_3^-+I^-)$ reference electrode.

REFERENCES

- 1) J. F. Coetzee, B. K. Deshmukh and C.-C. Liao, *Chem. Rev.*, **90**, 827 (1990).
- 2) K. Izutsu, T. Nakamura, T. Arai and M. Ohmaki, *Electroanalysis*, **7**, 884 (1995).
- 3) M. Ue, *Denki Kagaku*, **62**, 620 (1994).
- 4) M. Ue, *J. Electrochem. Soc.*, **141**, 3336 (1994).
- 5) M. Ue and S. Mori, *J. Electrochem. Soc.*, **142**, 2577 (1995).
- 6) M. Ue, *Electrochim. Acta*, **39**, 2083 (1994).
- 7) M. Ue, K. Ida and S. Mori, *J. Electrochem. Soc.*, **141**, 2989 (1994).
- 8) M. Ue, T. Sato, H. Asahina, K. Ida and S. Mori, *Denki Kagaku*, **60**, 480 (1992).
- 9) M. Ue, T. Sato and M. Takeda, *Denki Kagaku*, **61**, 1080 (1993).
- 10) M. Ue, K. Shima and S. Mori, *Electrochim. Acta*, **39**, 2751 (1994).
- 11) M. Ue, S. Sekigawa, M. Takeda and S. Mori, *Denki Kagaku*, **63**, 63 (1995).
- 12) M. Ue, M. Takeda, Y. Suzuki and S. Mori, *J. Power Sources*, in press (1996).
- 13) J. F. Coetzee, T.-H. Chang, B. K. Deshmukh and T. Fonong, *Electroanalysis*, **5**, 765 (1993).
- 14) K. Izutsu, I. M. Kolthoff, T. Fujinaga, M. Hattori and M. K. Chantooni, Jr., *Anal. Chem.*, **49**, 503 (1977).
- 15) K. Izutsu, T. Nakamura and S. Hiraoka, *Chem. Lett.*, 1843 (1993).
- 16) K. Izutsu and M. Ohmaki, *Talanta*, **43**, 643 (1996).
- 17) A. P. Kreshkov, *Talanta*, **17**, 1029 (1970).
- 18) J. F. Coetzee and C. W. Gardner, Jr., *Anal. Chem.*, **54**, 2625 (1982).
- 19) A. Kato, Y. Konno, Y. Yanagida, M. Yamasato, T. Taguchi and R. Motohashi, *Anal. Sci.*, **7**, 1577 (1991).
- 20) J. F. Coetzee and C. W. Gardner, Jr., *Anal. Chem.*, **54**, 2530 (1982).
- 21) M. Ue and J. F. Coetzee, unpublished results.
- 22) B. K. Deshmukh, S. Siddiqui and J. F. Coetzee, *J. Electrochem. Soc.*, **138**, 124 (1991).
- 23) B. K. Deshmukh and J. F. Coetzee, *J. Electrochem. Soc.*, **138**, 133 (1991).
- 24) E. Kirowa-Eisner and E. Gileadi, *J. Electroanal. Chem.*, **25**, 481 (1970).