doi:10.1246/cl.2011.1423

AC Electrochemical Stability of Ionic Liquids

Fulong Yang,[1] Zuopeng Li,[1] Shiguo Zhang,[1] Qinghua Zhang,[1] Xiaodong Hu,[2] Xiaoping Zhang,*[2] and Youquan Deng*[1]
[1]*Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics,*
Chinese Academy of Sciences, Lanzhou 730000, P. R. China
[2]*School of Information Science and Engineering, Lanzhou University, Lanzhou 730000, P. R. China*

(Received June 28, 2011; CL-110542; E-mail: ydeng@licp.cas.cn)

AC electrochemical windows (AC EWs) of ILs were first investigated on Pt, glass carbon (GC), and Au electrodes with frequency ranging from 20 to 100 Hz. The result showed that the AC EW of ILs was much wider than the DC EWs, and the AC EW increased markedly with frequency and with electrode in the order of GC > Pt > Au. Moreover, AC CVs of ILs provide not only different AC EWs but also different current density under identical voltage that are both structure-dependent.

Room-temperature ionic liquids (ILs) have been widely used as potential electrolytes in electrochemical applications, such as dye-sensitized solar cell,[1] Li ion batteries,[2] supercapacitors,[3] electrodeposition,[4] and electrosynthesis.[5] A key criterion for ILs in such applications is the electrochemical stability of ILs toward a particular electrode. Generally, the electrochemical stability is denoted as "electrochemical window" (EW) estimated by cyclic voltammetry (CV) or linear sweep voltammetry (LSV).[6] Usually, ILs have significantly wider EWs than traditional aqueous electrolytes.[7] For example, EW of *N*-butyl-*N*-methylpyrrolidinium nonaflate on Pt electrode is as wide as 6.0 V.[8] The wide EWs of ILs open the door to electrodeposit metals or semiconductor and battery application.

Although studies to date are largely focused on the DC electrochemical stability or DC EWs, ILs are actually used in AC cases. For example, it was recently reported by us and other groups that electrowetting of ILs under AC electric field showed greatly enhanced, sensitive, and reversible contact-angle modulation in comparison to that under DC electric field.[9] Ono et al. developed a high-mobility, low-power, and fast-switching organic field-effect transistor using ILs.[10] Meanwhile, the novel photoelectric characteristics of ILs was studied in our group under AC voltages.[11] These uses call for in-depth investigation of AC electric stability and AC EWs of ILs for further development of the AC application of ILs. Unfortunately, up to now the AC electrochemical properties of ILs remain poorly understood. We herein investigated the AC electrochemical stability of ILs on different electrodes with variable AC frequency.

Different from the DC EW that was defined as the "cut-off current density,"[6] an attempt of establishing an AC EW for ILs was preliminarily made using $[BMIm]BF_4$ on Pt electrode as a typical case. With the experiment set-up as shown in Figure 1, the *I*–*V* curve of $[BMIm]BF_4$ on Pt electrode and at a fixed frequency was determined. As shown in Figure 2b, the current through the surface of the electrode first quickly increased with voltage and then abruptly decreased at a certain value. This inflexion could be related to passivation caused by the decomposition of ILs on electrode surface, since some yellow or brown substance appeared on Pt surface. The inflexion voltage thus can be directly denoted as the AC EW of ILs.

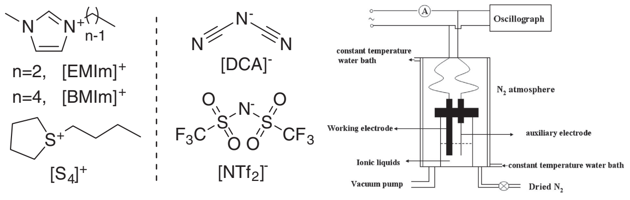

Figure 1. (Left) Structures of ILs investigated. (Right) Experiment set-up for measuring AC EW of ILs (for more details see SI[12]).

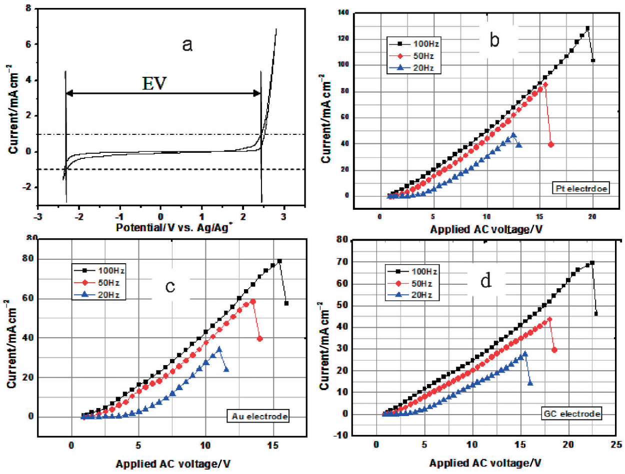

Figure 2. (a) CVs of $[BMIm]BF_4$ on 2-mm-diameter Pt electrode, scan rate $50\,mV\,s^{-1}$; b–d, AC *I*–*V* curve of $[BMIm]BF_4$ on 2-mm-diameter Pt (b), Au (c), and GC (d) electrode with frequency of 20, 50, and 100 Hz, the auxiliary electrode: Pt wire. The AC current is root-mean-square.

The *I*–*V* curves of $[BMIm]BF_4$ on different electrodes and at variable frequency is given in Figure 2 and Table 1, together with the DC result for comparison. Obviously, the AC EWs of ILs in all cases were greatly wider than the corresponding DC EWs. For example, AC EW of ILs on Pt electrode and at 20 Hz is as wide as 11.9 V, nearly three times as its corresponding DC EW. Moreover, increasing the AC frequency was found to facilitate strong electrochemical stability. For example, the AC EWs of ILs on Pt electrode increased markedly from 12.0 to 17.9 V with increasing the frequency from 20 to 100 Hz. Electrode materials were found to have great impact on the AC EWs of ILs. As seen in Figures 2c and 2d, the AC EWs on different electrodes with identical frequency followed the trend GC > Pt > Au, consistent with the DC electrochemical stability.

Table 1. AC EW and DC EW (/V) of ILs on Pt, Au, and GC electrodes with frequency of 20, 50, and 100 Hz at 25 °C

		[EMIm]BF$_4$	[BMIm]BF$_4$	[BMIm]PF$_6$	[BMIm]NTf$_2$	[S$_4$]DCA
c^a		47	176	46	59	191
σ^b		15.4	3.6	1.1	3.2	7.6
Pt	20 Hz	11.9	12.0	16.7	12.4	11.5
	50 Hz	15.2	15.6	20.0	17.1	13.8
	100 Hz	18.8	19.7	>36.0^c	19.2	16.1
	DC	4.2	4.6	4.6	4.4	3.0
Au	20 Hz	11.0	11.2	14.2	12.0	10.8
	50 Hz	13.4	13.8	16.0	13.5	13.1
	100 Hz	15.2	15.9	19.5	18.3	14.2
	DC	3.8	3.9	4.3	4.1	2.8
GC	20 Hz	15.3	15.5	19.0	16.1	12.5
	50 Hz	17.8	18.5	24.6	19.6	15.0
	100 Hz	22.5	23.6	>36.0^c	20.9	18.1
	DC	4.5	4.7	4.9	4.8	3.2

^{a}Refers to water content (ppm). ^{b}Refers to conductivity of ILs (mS cm^{-1}). ^{c}Refers to the data out of range of instrument determination.

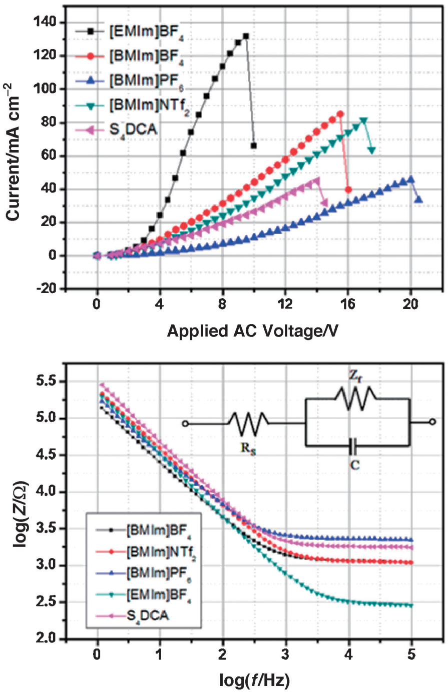

Figure 3. (Top) AC *I*–*V* curves of various ILs on Pt electrode at 50 Hz. (Bottom) Characteristic curves of impedance of different ILs.

To further investigated the effect of structure of ILs on their AC electrochemical stability, the AC EWs of a series of ILs with different cations and anions were measured on Pt, Au, and GC electrodes with variable frequency (20, 50, and 100 Hz). The result is given in Table 1, together with the comparative values of DC EWs. The conclusion derived from [BMIm]BF$_4$ can be extended to other ILs studied in this work. All ILs exhibited strongly structure-dependent AC EWs, which are remarkably higher than the corresponding DC EWs.

An attractive feature of AC EWs differing from DC EWs is that it provides not only the structure-dependent AC EWs but also different current density. The AC *I*–*V* curves of five ILs on Pt electrode at 50 Hz were tested and given in Figure 3. Under identical voltage, the order of current density through Pt electrode was [EMIm][BF$_4$] > [BMIm][BF$_4$] > [BMIm][NTf$_2$] > [S$_4$][DCA] > [BMIm][PF$_6$]. This is rather similar to the change trend of ionic conductivity (Table 1), wherein ILs with high conductivity give high current density, except that of [S$_4$][DCA]. Of the ILs investigated, [EMIm][BF$_4$] exhibited the highest current density due to its remarkably highest ionic conductivity. Although the conductivity of [S$_4$][DCA] was as high as 7.6 mS cm^{-1}, its current density on Pt electrode is fairly low, which could be due to passivation occurring on Pt electrode induced by [S$_4$][DCA] degradation. It should be noted that the electrode materials have also great effect on the AC current density for ILs under the same frequency and voltage, as shown in Figure 2 for [BMIm][BF$_4$]. It could be concluded that the electrochemical response on Pt, Au, and GC electrodes of electrohemical active substance is different in previous studies,[5] which could be responsible for the above-mentioned phenomena. Different frequency also caused different current density within AC EWs. This phenomenon can be illustrated by the Bodes of ILs, as shown in Figure 3b. The module Z showed a plateau region at about 106–103 Hz and increased linearly 1 Hz for [BMIm][BF$_4$], [BMIm][PF$_6$], [BMIm][NTf$_2$], and [S$_4$][DCA]. The frequency range of ILs studied corresponded to capacitive behavior of electrode/ILs interface. Therefore, the frequency studied in this work of 20–100 Hz was the increased linearly part of the Bode, thus the current could increase with the frequency increasing.

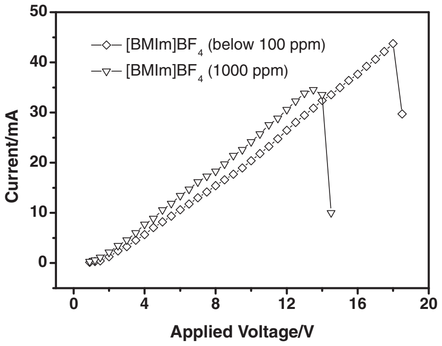

Figure 4. Water influence on the AC EW of [EMIm]BF$_4$ (GC electrode, 50 Hz).

The presence of water can significantly influence the AC EW of ILs (Figure 4). The AC EWs of [BMIm][BF$_4$] with water content of 1000 ppm and below 100 ppm on GC electrode are 14.0 and 18.5 V, respectively, which are similar to the case of DC EWs. Note that water content of ILs below 100 ppm was found to have no obvious influence to the AC EW.

Although detailed mechanism of the enhanced AC electrochemical stability of ILs is not clear to us at this current stage, it can be conjectured that when the AC electric field was applied, the cathode or anode was frequently changed, which prevent the oxidation (anion) or reduction (cation) of ILs.

In conclusion, the AC electrochemical stability of ILs on Pt, GC, and Au electrodes with frequency ranging from 20 to 100 Hz was first studied. The AC electrochemical stability or AC EWs of ILs have been estimated according to inflexion point due to the electrode surface passivation caused by ILs degradation. The AC EWs of ILs became greatly wider than DC EWs and provide not only voltage but also current density. AC EWs of ILs were found to be affected by the structure of ILs, applied frequency and electrodes. The study of AC electrochemical stability of ILs could provide fundamental data for further study and application of ILs in AC electrochemistry.

The authors thank the National Natural Science Foundation of China (Nos. 21173240 and 21103208) for financial support.

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12 Synthesis, purification, and electrochemical measurement of ILs are available on Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.