# Refined Method for Predicting Electrochemical Windows of Ionic Liquids and Experimental Validation Studies

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ABSTRACT: A combined classical molecular dynamics (MD) and ab initio MD (AIMD) method was developed for the calculation of electrochemical windows (ECWs) of ionic liquids. In the method, the liquid phase of ionic liquid is explicitly sampled using classical MD. The electrochemical window, estimated by the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), is calculated at the density functional theory (DFT) level based on snapshots obtained from classical MD trajectories. The snapshots were relaxed using AIMD and quenched to their local energy minima, which assures that the HOMO/LUMO calculations are based on stable configurations on the same potential energy surface. The new procedure was applied to a group of ionic liquids for which the ECWs were also experimentally measured in a self-consistent manner. It was found that the predicted ECWs not only agree with the experimental trend very well but also the values are quantitatively accurate. The proposed method provides an efficient way to compare ECWs of ionic liquids in the same context, which has been difficult in experiments or simulation due to the fact that ECW values sensitively depend on experimental setup and conditions.
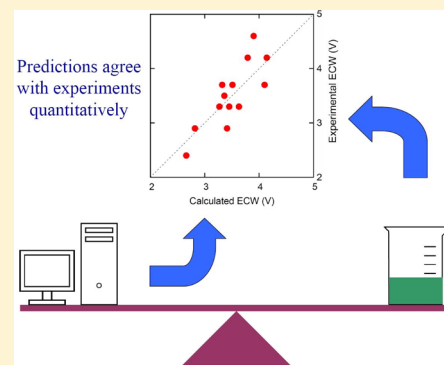
1. INTRODUCTION

Ionic liquids (ILs) are salts that have melting temperature below 100 °C. Many ILs have unique properties such as negligible vapor pressure, nonflammability, and good ionic conductivity. Their promising potential for applications in various areas has stimulated extensive studies on this group of compounds.[1−7] The ability to tune the properties of an IL by combining different cations and anions earned ILs the name of "designer solvent".

Like other salts, ILs are composed of cations and anions that can conduct ions in their liquid phases. Naturally, serving as a solvent or electrolyte in electrochemical devices is one potential application of ionic liquids, and their electrochemical stability plays an essential role in such applications.[8,9] As such, the electrochemical window (ECW), the voltage range between which the solvent does not get oxidized nor reduced, has been the focus of many experimental studies.[10−19]

Compared with the extensive experimental studies on ECW, relatively few theoretical studies are available in the literature. In 1996, Koch and coworkers measured the ECW for a group of 1,2-dimethyl-3-propylimidazolium-based ionic liquids. The authors found that the measured anodic limits correlated well with the calculated highest occupied molecular orbital (HOMO) energies.[20] Similarly, Buijs and coworkers observed a correlation between the experimental ECW with the lowest unoccupied molecular orbital (LUMO) calculated at either density functional theory (DFT) level or semiempirical level.[21] While most previous studies are based on calculations in the vacuum, Ceder and coworkers introduced a procedure in which the liquid phase is explicitly considered.[22] This procedure combines classical molecular dynamics (MD) simulation and DFT calculation with periodic boundary conditions. The snapshots sampled in the classical MD simulation were used as input for DFT calculations in which the HOMO and LUMO energies were calculated. The cathodic and anodic limits were assumed to be properly represented by the LUMO and HOMO energies, respectively, and the ECW was calculated as their difference. The procedure was applied to six common ionic liquids, and the results agree with the available experimental trend, although the absolute values are systematically underestimated. According to the authors, this is due to the use of relatively cheap but inaccurate DFT theory.[22]

It is worth mentioning that ECWs measured in experiments can be affected by many factors such as the electrode material, cutoff current, and impurities.[16,23−28] As a result, the ECW for a given IL can vary significantly depending on the experimental details. For example, reported experimental ECWs of 1-n-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM][PF_6]$) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ($[EMIM][TF_2N]$), two well-studied ionic liquids, are summarized in Table 1. As seen in the Table, for both ILs, the reported ECW values vary by >1 V. This makes it difficult to compare results from different research groups or results with different experimental setups from the same group. The large deviation in experimental results also makes it hard to verify a computational procedure for ECW prediction.

In this work, we present a ECW calculation method that is developed based on Ceder's combined MD and DFT procedure.[22] The details of the new procedure as well as

Table 1. Summary of Experimental Electrochemical Windows (ECW, in V) for $[BMIM][PF_6]$ and $[EMIM][TF_2N]$ from the Literature[a]

IL	ECW (V)	literature
$[BMIM][PF_6]$	4.2	ref 24
	4.4	ref 10
	3.2	ref 12
	4.8	ref 28
	5.2	ref 17
$[EMIM][TF_2N]$	4.5	ref 10
	4.0	ref 12
	4.2	ref 28
	5.0	ref 17

[a]Different values reported by different authors are likely due to the use of different electrode materials which is well known to influence the results, the impurities such as water content in the sample, or even cutoff current in the experiments.

experimental details will be described in the next section. The robustness and accuracy of the method was verified against previous and new experimental results.

2. SIMULATION PROCEDURE

Following previous work,[22] the cathodic limit (V_{CL}) and anodic limit (V_{AL}) are represented by the calculated LUMO and HOMO energies, respectively, and the ECW is estimated from their difference

$$ECW = V_{AL} - V_{CL} = \frac{-\varepsilon_{HOMO}}{e} - \frac{-\varepsilon_{LUMO}}{e}$$
$$= \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{e} \quad (1)$$

The HOMO and LUMO for each IL was calculated using a combined classical MD simulation and ab initio MD (AIMD) procedure. The classical MD simulation followed similar procedures described in our previous publications.[29,30] In brief, the simulation box contains eight ion pairs, which have been reported to be the smallest size still able to faithfully mimic the liquid phase.[31] As described later, tests were run with larger systems containing 12 and 16 ion pairs, and the results were statistically the same for all three size systems. The intra- and intermolecular interactions were described by the general Amber force field (GAFF).[32] The atomic partial charge on each atom was derived using the RESP procedure[33] based on the optimized structure of each isolated ion at the B3LYP/6-311+ +G(d,p) level using the Gaussian 09 package.[34] For each IL, a 2 ns classical MD simulation in the isothermal−isobaric (NPT) ensemble was carried out at 300 K and 1 atm pressure. The NPT simulation was followed by a 2 ns simulation in the canonical (NVT) ensemble. The first nanosecond of the NVT trajectory was considered equilibration and discarded. Ten snapshots were taken from the second nanosecond trajectory at 100 ps intervals. All classical MD simulation was carried out using the package LAMMPS.[35]

In Ceder's procedure,[22] the snapshots obtained in this manner are directly used for HOMO/LUMO calculation at the DFT level without further equilibration or geometry optimization. Their procedure will be referred to as the "AIMD-sp" method hereafter. ("sp" stands for single-point calculation.)

Because the potential energy surfaces (PESs) described by the applied classical force field and the high-level DFT theory are likely different, the snapshots sampled in classical MD simulation do not necessarily represent stable configurations at the DFT level. We therefore extended Ceder's procedure such that each snapshot from the classical MD simulation was relaxed for 300 steps at 300 K using Car−Parrinello-type molecular dynamics (CPMD) in the package CPMD.[36] The final configuration was then quenched to the potential energy minimum in 3000 steps using simulated annealing. In the CPMD simulation, the PBE functional[37,38] was used (unless otherwise specified) with the norm-conserving pseudopotential of the Troullier−Martins form.[39] A time step of 4 au was used, and the energy cutoff was set to 90 Ry, consistent with our previous studies on ionic liquids.[30] The HOMO and LUMO energies for the quenched configurations were then calculated using the package CPMD at the same level of theory. This revised procedure will be called "AIMD-min" method hereafter.

3. EXPERIMENTAL METHODS

All ILs for which ECWs were measured were synthesized in our laboratory. ILs were dried under vacuum at ∼50 °C for a minimum of 48 h before use to remove impurities and residual water. The water content of all ILs was determined using a Brinkman 831 Karl Fischer coulometer (±3%) and was <300 ppm after purification.

The ECW measurement of ILs was carried out by cyclic voltammetry using a Radiometer Analytical VoltaLab50 potentiostat. IL samples were loaded into a conventional three-electrode cell under a nitrogen atmosphere (M. Braun dry glovebox) at ambient temperature. Glassy carbon (BASi, $d = 3$ mm) was used as the working electrode. A platinum wire was mounted in the cell cap as a counter electrode. The nonaqueous reference electrode was composed of a silver wire immersed in 0.1 M silver trifluoromethanesulfonate (AgOTf) in a 1-n-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ($[HMIM][TF_2N]$) solution with <20 ppm water content. The supporting electrolyte in the reference glassy tube was separated from the test IL solution by a Vycor glass frit to prevent contamination and junction potential. All measurements were carried out at room temperature in the glovebox with 100 mV/s scan rate. 1.0 mA/cm^2 cutoff current was used to determine the anodic potential limit (V_{AL}) and cathodic potential limit (V_{CL}), and the ECW was calculated as follows: $ECW = V_{AL} - V_{CL}$. The uncertainty of the measured ECWs were estimated to be within ±0.1 V.

Table 2. Summary of Predicted and Experimental Electrochemical Windows (ECW, in V) for $[BMIM][PF_6]$, $[BMIM][BF_4]$, and $[BMIM][TF_2N]$

IL	AIMD-min	AIMD-sp (this work)	AIMD-sp (ref 22)	exp.
$[BMIM][PF_6]$	4.66 ± 0.03	4.16 ± 0.02	3.59	3.2−5.2[10,12,17,24,28]
$[BMIM][BF_4]$	4.49 ± 0.05	4.05 ± 0.06	3.63	4.1−4.6[10,17,24,28]
$[BMIM][TF_2N]$	4.19 ± 0.05	2.35 ± 0.10	3.62	4.3−4.6[24,28]

4. RESULTS AND DISCUSSION

4.1. Validation of Calculation Procedure. The proposed ECW calculation procedure was first applied to three well-studied ILs, [BMIM][PF$_6$], [BMIM][BF$_4$] (1-n-butyl-3-methylimidazolium tetrafluoroborate), and [BMIM][TF$_2$N], which were also studied by Ceder and coworkers.[22] The calculated results are shown in Table 2 and compared with previous experimental results. For all three ILs, the calculated ECWs using the AIMD-min procedure agree with experimental ranges very well. The results calculated by following the AIMD-sp procedure are also provided. AIMD-sp results for all ILs are smaller than those obtained with the AIMD-min method. For [BMIM][PF$_6$], the AIMD-sp result is in reasonable agreement with the experimental values. For [BMIM][BF$_4$], the calculated result is close to the minimum value reported in experiments. For [BMIM][TF$_2$N], however, it is at least 1.95 V lower than any experimental results. The large difference suggests that without equilibration at the AIMD level the AIMD-sp procedure tends to underestimate the stability of the compounds, which is likely due to the relatively high energy of the configurations on the PES. The results reported in Ceder's work[22] are also included in Table 2. Note that in Ceder's work ECW values around 3.6 V were predicted for all three ILs, different from the values obtained here. The differences between the current AIMD-sp calculation and their results are likely due to the differences in the applied classical force field and other details in the simulation setup, which would cause differences in the sampled PES, indicating the importance of relaxing and quenching the sampled structures at the theoretical level at which HOMO/LUMO was calculated.

A second test was carried out to examine the sensitivity of the proposed procedure on the liquid phase density obtained from classical MD simulation. For [BMIM][PF$_6$], the applied force field predicted a liquid density of 1.360 g/cm^3 at 300 K, which agrees with the experimental result of 1.359 g/cm^3 very well.[40] In general, however, densities predicted with classical force fields carry an error of up to 5%.[30] To test the robustness of the AIMD-min procedure with respect to the accuracy of the classical MD simulation, we manually adjusted the size of the equilibrated simulation box by ±5% and re-equilibrated it for 2 ns to artificially change the liquid density. The ECW calculation was then carried out, and the results are summarized in Table 3.

Table 3. Study of Sensitivity of the Calculated Electrochemical Windows (ECW, in V) on Liquid Phase Density for [BMIM][PF$_6$]

	density (300 K) (g/cm^3)	ECW (V)
calc.	1.360	4.66 ± 0.03
	1.432 (+5%)	4.68 ± 0.03
	1.295 (−5%)	4.61 ± 0.04
exp.	1.359[40]	3.2−5.2[10,12,17,24,28]

As shown in the Table, with 5% higher or lower density, the ECW was found to be insensitive to the liquid density in the tested range, suggesting that the method is robust with regards to the starting classical structure.

The third test carried out was on the length of equilibration at the AIMD level. Ionic liquids usually have high viscosities and the dynamics are slow. Therefore, the sampling of their PES requires extremely long simulation times. In the method used in this work, classical MD simulation was used to sample

the PES. The goal of the equilibration and quenching at the AIMD level is to make sure that the configuration in the HOMO/LUMO calculation is stable on the PES and is a reasonable representation of the PES at the same theoretical level. AIMD simulations are relatively expensive. To save simulation time, shorter AIMD equilibration is always preferred.

For each snapshot of [BMIM][PF$_6$] obtained from the classical MD simulation, an AIMD relaxation was carried out for 300, 500, and 1000 steps, respectively. The equilibrated structure was then quenched in 3000 steps of simulated annealing during which the atomic velocities were scaled by 0.95 from the previous step. The HOMO/LUMO energy was calculated for the structure after equilibration but before quenching as well as after quenching. The results are summarized in Table 4. Without quenching the configurations

Table 4. Summary of Calculated Electrochemical Windows (units: V) for [BMIM][PF$_6$] with Different Length of AIMD Relaxation Steps Using the AIMD-min Procedure

equ. steps	after equ.	after quenching (3000 steps)
0	4.16 ± 0.02	
300	3.95 ± 0.05	4.66 ± 0.03
500	4.32 ± 0.06	4.63 ± 0.04
1000	4.29 ± 0.04	4.70 ± 0.03
exp.	3.2−5.2[10,12,17,24,28]	

the calculated ECWs fluctuate from 4.16 V with zero steps of equilibration (AIMD-sp) to 3.95 after 300 steps of equilibration before stabilizing at ~4.3 V after 500 steps or longer equilibration. For the quenched structures, almost the same ECWs of 4.6 to 4.7 V were obtained independent of the equilibration length. Note that for this particular IL the fluctuation in the calculated ECWs is relatively small even without structure quenching, whereas the difference between nonquenched and quenched structures is large (up to 0.71 V). Larger fluctuations were observed for other ILs. For example, for triethylbutylphosphonium 1,2,4-triazolide ([P$_{2224}$]-[124triz]), the fluctuation in ECWs is as large as 0.6 V if no structure quenching was carried out, but the results based on quenched structures are always stable. In the rest of the work, equilibration of 300 steps is carried out before a configuration is quenched.

The last test studied the effect of the system size. Previous studies[31] have reported that eight ion pairs are sufficient for AIMD modeling of liquid properties. Simulation boxes containing 12 and 16 pairs of [BMIM][PF$_6$] were set up, and simulations were carried out by following the same procedure previously described. The calculated ECWs are summarized in Table 5. As shown in the Table, the results using the AIMD-min method are statistically equivalent. The deviation is slightly larger in the results using the AIMD-sp method, but the differences are small. Given the computational expense of the

Table 5. Calculated Electrochemical Windows (units: V) for [BMIM][PF$_6$] Using Different Box Sizes

pairs of IL in box	AIMD-sp	AIMD-min
8	4.16 ± 0.02	4.66 ± 0.03
12	4.04 ± 0.06	4.61 ± 0.05
16	3.97 ± 0.04	4.53 ± 0.04

AIMD simulations, systems with eight ion pairs were used to compute ECWs for all ILs in this work.

4.2. ECW of 1,2,4-Triazolide and 2-(Cyano)pyrrolide Ionic Liquids. In a typical electrochemical application, in addition to large ECW, higher ionic conductivity and lower viscosity are usually preferred. Previous studies have shown that ILs with planar ions tend to show better performance for Li+ conductivity.[41] In light of this finding, a group of ILs were synthesized that had two different planar anions: 1,2,4-triazolide ([124triz]) and 2-(cyano)pyrrolide ([CNPyr]). These were combined with seven different cations, triethylbutylphosphonium ([P_{2224}]), trihexyl(tetradecyl)phosphonium ([P_{66614}]), (methyloxymethyl)triethylphosphonium ([P_{222mom}]), triethyl((2-methoxyethoxy)methyl) phosphonium (([P_{222mem}]), 1-butyl-1-methylpyrrolidinium ([PY_{14}]), 1-butyl-3-methylimidazolium ([BMIM]), and 1-ethyl-3-methylimidazolium ([EMIM]) to form 13 different ionic liquids. [P_{222mom}]-[124triz] is a solid at room temperature. Various dynamic and electrochemical properties were measured for each of these ILs. Part of the results were presented in a previous publication.[42] The ECW results will be the focus of the current work, and other results will be presented in another publication.

The ECW calculation procedure previously described was applied to these ILs, and the results are compared with experimental values in Table 6. As shown in the Table, the

Table 6. Calculated and Experimental Electrochemical Windows (units: V) for a Group of Ionic Liquids Containing 2-(Cyano)pyrrolide and 1,2,4-Triazolide Anions[a]

IL	AIMD-sp	AIMD-min	exp.
[P_{2224}][CNPyr]	3.10 ± 0.02	3.32 ± 0.05	3.7
[P_{2224}][124triz]	3.26 ± 0.01	3.90 ± 0.04	4.6
[P_{222mom}][CNPyr]	2.95 ± 0.02	3.45 ± 0.03	3.3
[P_{222mom}][124triz]	3.19 ± 0.02	4.01 ± 0.04	
[P_{222mem}][CNPyr]	3.03 ± 0.02	3.36 ± 0.05	3.5
[P_{222mem}][124triz]	3.29 ± 0.02	4.15 ± 0.04	4.2
[P_{66614}][CNPyr]	3.28 ± 0.01	3.50 ± 0.04	3.7
[P_{66614}][124triz]	3.25 ± 0.02	3.79 ± 0.06	4.2
[EMIM][CNPyr]	2.17 ± 0.01	2.66 ± 0.03	2.4
[EMIM][124triz]	2.49 ± 0.02	3.41 ± 0.05	2.9
[BMIM][CNPyr]	2.23 ± 0.02	2.82 ± 0.02	2.9
[BMIM][124triz]	2.34 ± 0.02	3.27 ± 0.06	3.3
[PY_{14}][CNPyr]	3.48 ± 0.02	3.63 ± 0.05	3.3
[PY_{14}][124triz]	3.67 ± 0.02	4.10 ± 0.05	3.7
rmsd	0.67	0.34	

[a]Experimental ECWs for the last eight ILs were taken from ref 42. Note that the AIMD-min procedure is recommended.

calculated ECWs using the AIMD-min method generally agree with experimental results very well. With the largest error found to be 0.7 V for [P_{2224}][124triz], the deviation for most other ILs is ~0.3 V or smaller. The root-mean-square deviation (rmsd) was calculated to be 0.34 V. The overall good agreement is clearly seen by the correlation shown in Figure 1. Consistent with experimental results, the predicted ECWs for the phosphonium ILs are larger than imidazolium-based ILs. PY_{14}-based ILs also have larger ECWs than imidazolium-based ILs. These observations are consistent with previous reports as well.[8,16] It is interesting to note that from both experimental measurements and the calculations, when paired with the same cation, [124triz] ILs were found to have larger ECWs than the [CNPyr] counterpart by an average of 0.5 to 0.6 V. These
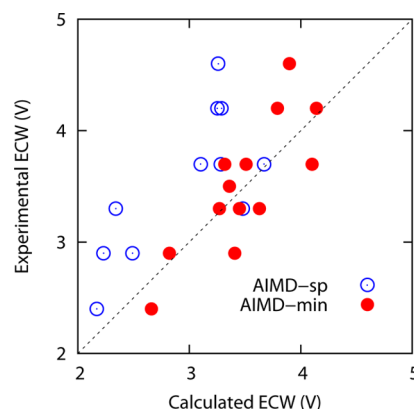

Figure 1. Correlation between predicted and experimental electrochemical windows (units: V) of a group of ionic liquids containing 2-(cyano)pyrrolide and 1,2,4-triazolide anions.

results suggest that the proposed AIMD-min method is not only able to predict the ECW trends qualitatively but also can get the values quantitatively correct. This is important to understand the complicated electrochemical process in these compounds for the design of better electrolytes.

The results obtained following the AIMD-sp procedure (using the same force field and DFT setup as in AIMD-min) are also shown in Table 6 and plotted in Figure 1. Similar to the case of [BMIM][PF_6], relative to the experimental values, the AIMD-sp procedure tends to underestimate the ECWs systematically. The rmsd was estimated to be 0.67 V, about double that in AIMD-min results. The difference between [124triz] and [CNPyr] ILs with the same cation is also underestimated with the average difference being <0.2 V.

4.3. ECW of Other Ionic Liquids. In addition to previously mentioned [CNPyr] and [124triz] ILs, the proposed method was also applied to other ILs. For most of these ILs, large ECWs have been reported previously based on various experimental measurements. As previously discussed, it is hard to make direct comparison with experiments carried out by different groups due to the inherent variability in the results. By applying the same calculation procedure to these ILs, their ECWs are brought to the same context and direct comparison is possible. The calculated results are shown in Table 7 along with available experimental data.

As shown in the Table, for most of the ILs, the calculated ECWs agree with the available experimental results reasonably well, although deviations larger than 1 V are observed in some cases. Relatively large ECWs were predicted for all of these ILs. Consistent with experimental observations, ILs with phosphonium-based or aliphatic (PY_{14}) cations or the TF_2N anion generally show large ECWs. The combination of phosphonium-based cations or [PY_{14}] with [TF_2N], for example, [P_{2224}]-[TF_2N], [P_{2225}][TF_2N], [P_{2228}][TF_2N], and [PY_{14}][TF_2N], all have ECWs larger than 5 V. [Choline][Cl] is one of the ILs that has been applied in the electrochemical industry.[43] An ECW of 5.06 V was predicted for this IL, which is larger than many others studied in this work, suggesting that this is a stable IL. Under certain experimental environments, [EMIM][B-(CN)$_4$] has been reported to be stable even with a very high potential.[18] In the current study, an ECW of 4.65 V was predicted, which is similar to other ILs in Table 7.

Table 7. Calculated Electrochemical Windows (units: V) Using the AIMD-min Procedure for ILs with Large ECWs Reported Previously

IL	calc.	exp.
[BMIM][PF$_6$]	4.66 ± 0.03	3.2−5.2[10,12,17,24,28]
[EMIM][B(CN)$_4$]	4.65 ± 0.04[a]	>6.0[18]
[BMIM][TF$_2$N]	4.19 ± 0.05	4.3−4.6[24,28]
[EMIM][TF$_2$N]	4.30 ± 0.05	4.0−5.0[10,12,17,28]
[P$_{2225}$][TF$_2$N]	4.95 ± 0.03	6.2[14]
[P$_{2228}$][TF$_2$N]	5.19 ± 0.07	6.2[14]
[P$_{222mem}$][TF$_2$N]	4.58 ± 0.05	5.3[14]
[P$_{222mom}$][TF$_2$N]	4.93 ± 0.03	5.3[14]
[PY$_{14}$][TF$_2$N]	5.01 ± 0.04	3.8−6.0[10,44,45]
[P$_{2224}$][TF$_2$N]	5.04 ± 0.04	
[Choline][Cl]	5.06 ± 0.06	

[a]The BLYP functional form was used in this calculation due to the lack of proper PBE pseudopotential of B atoms. The test was carried out on [EMIM][124triz], which shares the same cation and similar elements in anion. The calculated ECWs using the two functionals were found to be the same (3.41 ± 0.05 V for PBE and 3.44 ± 0.03 for BLYP), and we believe that the difference in functional forms does not affect the ECW results.

5. CONCLUDING REMARKS

In this work, an improved method to predict ECW for ionic liquids is described and tested. Different from previous methods, where single-point DFT calculations were run on structures obtained from classical MD simulations (AIMD-sp), the liquid-phase configurations obtained from classical MD simulation were relaxed at the ab initio level for a short period of time. The configurations were then quenched to their energy minimum on the ab initio PES. These extra steps ensure that the HOMO/LUMO analysis and subsequent ECW calculation are based on the stable structures at the same level of theory. We refer to this new methods AIMD-min.

A group of ionic liquids were synthesized, and their ECWs were measured using cyclic voltammetry. These ILs are formed with [124triz] or [CNPyr] anions and seven different phosphonium-, imidazolium-, and pyrrolidinium-based cations, which cover several of the most widely studied ILs. As expected, the ILs were found to be more stable in the AIMD-min method than in AIMD-sp method. In addition to the accurate prediction of the experimental trends that [124triz] ILs have larger ECWs than the corresponding [CNPyr] ones with the same cation and that imidazolium-based ILs have relatively smaller ECWs than phosphonium and pyrrolidinium ones, the predicted ECW values using the AIMD-min procedure also agree very well with the experimental results quantitatively. The proposed AIMD-min method was also found to be robust and insensitive to the quality of the classical force field as long as a reasonable force field is used, which is definitely an advantage because the development of an accurate classical force field itself can be a tedious task.

The proposed procedure was also applied to ILs that have been studied previously in different experimental setups. There is no doubt that the electrochemistry of ionic liquids is a complicated process. Depending on the particular application and experimental condition, the same IL can show different electrochemical stability. The calculation method described in this work, however, provides a reliable way to compare ECWs of different ILs in the same framework, which is an essential step for the understanding of electrochemical phenomenon in ionic liquids and will benefit their applications in related fields.

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■ REFERENCES

(1) Wasserscheid, P. Continuous reactions using ionic liquids as catalytic phase. *J. Ind. Eng. Chem.* **2007**, *13*, 325−338.
(2) Plechkova, N.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Rev.* **2008**, *37*, 123−150.
(3) Maginn, E. J. Molecular simulation of ionic liquids: current status and future opportunities. *J. Phys.: Condens. Matter* **2009**, *21* (37), 373101.
(4) Zhang, S.; Lu, X.; Zhang, Y.; Zhou, Q.; Sun, J.; Han, L.; Yue, G.; Liu, X.; Cheng, W.; Li, S. Ionic Liquids and Relative Process Design. In *Molecular Thermodynamics of Complex Systems*; Lu, X. Hu, Y., Eds.; Structure and Bonding 131; Springer: Berlin, **2009**; pp 143−191.
(5) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. *Chem. Rev.* **2011**, *111*, 3058−3576.
(6) Wendler, K.; Dommert, F.; Zhao, Y.; Berger, R.; Holm, C.; Delle Site, L. Ionic liquids studied across different scales: a computational perspective. *Faraday Discuss.* **2012**, *154*, 111−132.
(7) Wang, H.; Gurau, G.; Rogers, R. D. Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, *41*, 1519−1537.
(8) Galinski, M.; Lewandowski, A.; Stepniak, I. Ionic liquids as electrolytes. *Electrochim. Acta* **2006**, *51*, 5567−5580.
(9) Hapiot, P.; Lagrost, C. Electrochemical reactivity in room-temperature ionic liquids. *Chem. Rev.* **2008**, *108*, 2238−2264.
(10) Lewandowski, A.; Stepniak, I. Relative molar Gibbs energies of cation transfer from a molecular liquid to ionic liquids at 298.15K. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4215−4218.
(11) Xiao, L.; Johnson, K. E. Electrochemistry of 1-butyl-3-methyl-1H-imidazolium tetrafluoroborate ionic liquid. *J. Electrochem. Soc.* **2003**, *150*, E307−E311.
(12) Barisci, J. N.; Wallace, G. G.; MacFarlane, D. R.; Baughman, R. H. Investigation of ionic liquids as electrolytes for carbon nanotube electrodes. *Electrochem. Commun.* **2004**, *6*, 22−27.
(13) Sato, T.; Masuda, G.; Takagi, K. Electrochemical properties of novel ionic liquids for electric double layer capacitor applications. *Electrochim. Acta* **2004**, *49*, 3603−3611.
(14) Tsunashima, K.; Sugiya, M. Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes. *Electrochem. Commun.* **2007**, *9*, 2353−2358.
(15) Kanematsu, S.; Matsumoto, K.; Hagiwara, R. Electrochemically stable fluorohydrogenate ionic liquids based on quaternary phosphonium cations. *Electrochem. Commun.* **2009**, *11*, 1312−1315.
(16) Rogers, E. I.; Sljukic, B.; Hardacre, C.; Compton, R. G. Electrochemistry in room-temperature ionic liquids: potential windows at mercury electrodes. *J. Chem. Eng. Data* **2009**, *54*, 2049−2053.
(17) Lewandowski, A.; Swiderska-Mocek, A. Lithium-metal potential in Li$^+$ containing ionic liquids. *J. Appl. Electrochem.* **2010**, *40*, 515−524.

(18) Seki, S.; Serizawa, N.; Hayamizu, K.; Tsuzuki, S.; Umebayashi, Y.; Takei, K.; Miyashiro, H. Physicochemical and electrochemical properties of 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)-trufluorophosphate and 1-ethyl-3-methylimidazolium tetracyanoborate. *J. Electrochem. Soc.* **2012**, *159*, 967−971.

(19) Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X. Investigating the electrochemical windows of ionic liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106−112.

(20) Koch, V. R.; Dominey, L. A.; Nanjundiah, C. The intrinsic anodic stability of several anions comprising solvent-free ionic liquids. *J. Electrochem. Soc.* **1996**, *143*, 798−803.

(21) Buijs, W.; Witkamp, G.-J.; Kroon, M. C. Correlation between quantum chemically calculated LUMO energies and the electrochemical window of ionic liquids with reduction-resistant anions. *Int. J. Electrochem.* **2012**, *2012*, 589050.

(22) Ong, S. P.; Andreussi, O.; Wu, Y.; Marzari, N.; Ceder, G. Electrochemical windows of room-temperature ionic liquids from molecular dynamics and density functional theory calculations. *Chem. Mater.* **2011**, *23*, 2979−2986.

(23) Suarez, P. A. Z.; Selbach, V. M.; Dullius, J. E. L.; Einloft, S.; Piatnicki, C. M. S.; Azambuja, D. S.; de Souza, R. F.; Dupond, J. Enlarged electrochemical window in dialkyl-imidazolium cation based room-temperature air and water-stable molten salts. *Electrochim. Acta* **1997**, *42*, 2533−2535.

(24) Schroder, U.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J. Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids. *New J. Chem.* **2000**, *24*, 1009−1015.

(25) Buzzeo, M. C.; Hardacre, C.; Compton, R. G. Extended electrochemical windows made accessible by room temperature ionic liquid/organic solvent elecrolytes systems. *ChemPhysChem* **2006**, *7*, 176−180.

(26) Snook, G. A.; Best, A. S.; Pandolfo, A. G.; Hollenkamp, A. F. Evaluation of a Ag−Ag⁺ reference electrode for use in room temperature ionic liquids. *Electrochem. Commun.* **2006**, *8*, 1405−1411.

(27) Zhao, C.; Burrell, G.; Torriero, A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R.; Bond, A. M. Electrochemistry of room temperature protic ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 6923−6936.

(28) O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. Effect of water on the electrochemical window and potential limits of room-temperature ionic liquids. *J. Chem. Eng. Data* **2008**, *53*, 2884−2891.

(29) Zhang, Y.; Maginn, E. J. The effect of C2 substitution on melting point and liquid phase dynamics of imidazolium based-ionic liquids: insights from molecular dynamics simulations. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12157−12164.

(30) Zhang, Y.; Maginn, E. J. A simple AIMD approach to derive atomic charges for condensed phase simulation of ionic liquids. *J. Phys. Chem. B* **2012**, *116*, 10036−10048.

(31) Wendler, K.; Zahn, S.; Dommert, F.; Berger, R.; Holm, C.; Kirchner, B.; Delle Site, L. Locality and fluctuations: trends in imidazolium-based ionic liquids and beyond. *J. Chem. Theory Comput.* **2011**, *7*, 3040−3044.

(32) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and testing of a general amber force field. *J. Comput. Chem.* **2004**, *25*, 1157−1174.

(33) Bayly, C.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. A well-behaved electrostatic potential based method using charge restraints for deriving atomic charges: the RESP model. *J. Phys. Chem.* **1993**, *97*, 10269−10280.

(34) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B.; Petersson, H.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(35) Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **1995**, *117*, 1−19.

(36) CPMD, http://www.cpmd.org/, Copyright IBM Corp 1990−2008, Copyright MPI fur Festkorperforschung Stuttgart 1997−2001.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(38) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(39) Troullier, N.; Martins, J. L. Efficient pseudopotential for plane-wave calculations. *Phys. Rev. B* **1991**, *43*, 1993−2006.

(40) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(41) Liu, H.; Maginn, E. Effect of ion structure on conductivity in lithium-doped ionic liquid electrolytes: A molecular dynamics study. *J. Chem. Phys.* **2013**, *139*, 114508.

(42) Shi, C.; Quiroz-Guzman, M.; DeSilva, A.; Brennecke, J. F. Physicochemical and electrochemical properties of ionic liquids containing aprotic heterocyclic anions doped with lithium salts. *J. Electrochem. Soc.* **2013**, *160*, A1604−A1610.

(43) Abbott, A. P.; Ryder, K. S.; Konig, U. Electrofinishing of metals using eutectic based ionic liquids. *Trans. Inst. Met. Finish.* **2008**, *86*, 196−204.

(44) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. Pyrrolidinium imides: a new family of molten salts and conductive plastic crystal phases. *J. Phys. Chem. B* **1999**, *103*, 4164−4170.

(45) MacFarlane, D. R.; Sun, J.; Golding, J.; Meakin, P.; Forsyth, M. High conductivity molten salts based on the imide ion. *Electrochim. Acta* **2000**, *45*, 1271−1278.