

## Quantum chemical aided molecular design of ionic liquids as green electrolytes for electrodeposition of active metals

TIAN Guo-cai(田国才), ZHOU Xue-jiao(周雪娇), LI Jian(李 坚), HUA Yi-xin(华一新)

Faculty of Materials and Metallurgical Engineering, Kunming University of Science and Technology, Kunming 650093, China

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**Abstract:** Quantum chemical calculation was used to estimate the reduction potentials of 25 organic cations and the oxidation potentials of 11 anions. This information was used to select promising cations and anions for the preparation of ionic liquids as green electrolytes for electrodeposition of active metals. The reasonable linear correlations between the lowest unoccupied molecular orbital (LUMO) energies and the reduction potentials of cations, and the linear relationships between the oxidation potentials and the highest occupied molecular orbital (HOMO) energies of anions were obtained. The orders of electrochemical stability for cations and anions being obtained agree well with the experimental measurements. The suitable ionic liquids with sufficiently wide electrochemical windows for electrodeposition of active metals are suggested to be [Emim]NTf<sub>2</sub>, [Bmim]NTf<sub>2</sub>, [Bmim]BF<sub>4</sub>, [Bmim]PF<sub>6</sub>, [Bmim]CTf<sub>3</sub>, [Emim]BF<sub>4</sub>, [Emim]PF<sub>6</sub>, [Emim]CTf<sub>3</sub>.

**Key words:** ionic liquid; quantum chemical calculation; green electrolyte; electrodeposition; active metals; molecular design; electrochemical stability; electrochemical window

### 1 Introduction

The production value of active metals (such as aluminum, and magnesium) accounts for half that of the nonferrous metal, only lower than that of the steel, but its energy consumption is very high. The common method applied to obtaining active metals is the electrolysis of molten salts of active metals, which has many disadvantages such as high temperature, high energy consumption, serious equipment corrosion and high environmental pollution. Therefore, the development of new effective, low-temperature and environmentally-benign technologies for active metals processing to reduce energy consumption and to lower investment costs and the greenhouse gas emissions is an industrial demand and challenge for the 21st century[1]. The “green solvent” ionic liquids may offer potential as environmentally sensitive media and alternatives to active metals production processes.

Ionic liquids, also called room-temperature ionic liquids (ILs), are liquids composed completely of organic

cations and inorganic/organic anions[2–5]. They have been widely applied to many fields such as organic synthesis, catalysis, electrochemistry, bio-catalysis, material science, and separation processes [2–5] due to their unique properties such as very low or negligible vapor pressure, wide electrochemical window, high electrochemical stability and ion conductivity[3–5]. Preliminary studies have shown that ionic liquids have potential as solvents for metal recovery[6–8]. It was found that almost all of the metals can be electrodeposited in ionic liquids, principally Li, Na, Al, Mg and Ti[9–10]. It was shown that the electrodeposition of Al from ionic liquids can save 30%–50% energy consumption compared with the traditional process, and this technology has been strongly supported as an industrial technology project by the partners of University of Alabama, Albany Research Center, Century Aluminum Company, Secat Inc. and University of Kentucky, USA.

Variations in cations and anions can produce different kinds of ionic liquids and the properties of ionic liquids depend on the structure of ions. Therefore, ILs

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**Corresponding author:** TIAN Guo-cai; Tel: +86-871-5162008; E-mail: [tiangc@iccas.ac.cn](mailto:tiangc@iccas.ac.cn); [tiangc@kmust.edu.cn](mailto:tiangc@kmust.edu.cn)  
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are often referred as “designer solvents”[4]. However, in recent years, the number of possible cation and anion combinations has increased significantly so that a large number ( $10^{18}$ ) of ionic liquids could possibly exist[3–5]. The synthetic problem of being able to rationally design ambient temperature ionic liquids through variation of the anion and cation still remains to be thoroughly investigated, despite attempts to correlate structure with melting point. An important question is how to do and how we start from for a specific research? It is thus essential to develop a systematic method of selectively choosing a specific ionic pair, to be used as a predictive tool for rational design of specific ionic liquids.

A high electrochemical stability of the ionic liquid is very important for its electrochemical applications. The electrochemical stability of an ionic liquid is always manifested by the width of the electrochemical window[11]. The electrochemical window of a substance is the voltage range in which the substance doesn't get oxidized or reduced. In general, for a specific ionic liquid, the oxidation potential is determined by the voltage of the anion oxidation and the reduction potential is determined by the voltage of the cation reduction. It was shown that electrochemical oxidation potentials of several anions can be correlated with their respective highest occupied molecular orbital (HOMO) energies and electrochemical reduction potentials (reductive stability) can be correlated with the lowest unoccupied molecular orbital (LUMO) energy level for many organic molecules [12–15] and anions[16]. So, we can design the specific ionic liquids with the largest electrochemical windows for active metals electro-depositions.

In this work, quantum chemical calculations were used to predict the electrochemical stability of several cations and anions of ionic liquids. The correlations between the electrochemical oxidation potentials of several anions with their respective HOMO energies and the relationships between the electrochemical reduction potentials of various anions with their respective LUMO energy levels were studied. On basis of these quantum chemical calculations and correlations, some suitable ionic liquids were suggested as electrolytes for the electrodeposition of active metals.

## 2 Computational methods

All of the stable structures of cations and anions were optimized and all of calculations of the conformation energies, HOMO and LUMO levels were performed with the GAUSSIAN 03 program[17]. On the basis of the famous Hohenberg and Kohn theorems, the density functional theory (DFT) provides a sound basis for the development of computational strategies for obtaining information about the energetics, structure, and

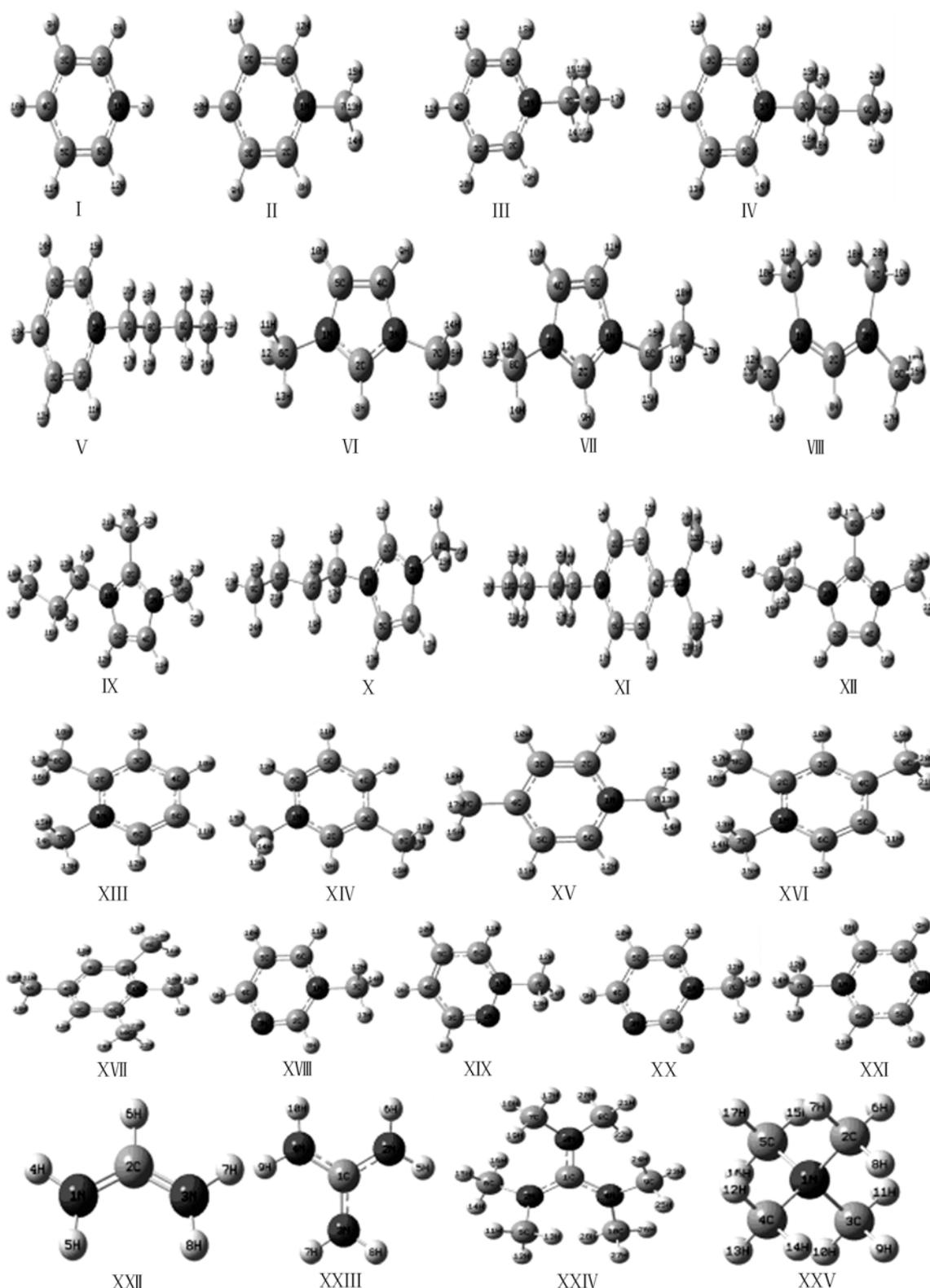
electron properties of atoms, molecules or ions at much lower costs than traditional *ab initio* wave function techniques (for example, Hartree-Fock, Møller-Plesset, configuration interaction, and coupled cluster theory) without accuracy loss[18–20].

The well-established Becke's three-parameter hybrid function coupled with the correlation function of Lee, Yang, and Parr (B3LYP)[21], which is known to be reliable, particularly for calculations of closed-shell stable molecules and ions system, was chosen in this work. The reasonably large basis sets 6-311 G\*\*[22] was used in all calculations. All of the stable structures of the cations and anions were obtained by the Berny analytical gradient optimization routines[23] and the convergence criteria were the same as the defaults in GAUSSIAN 03. All of the stable structures were verified carefully that there does not exist imaginary frequencies in their frequency calculations.

## 3 Results and discussion

It was previously found that a high energy level of the HOMO results in a less stable anion with respect to oxidation (it is easier to remove the electron from this orbital)[11, 24]. And it was assumed that a low energy level of the LUMO results in a less stable cation with respect to oxidation (it is easier to put an additional electron in this orbital). Therefore, it is expected that ionic liquids exhibit a large electrochemical window when the anion possesses a low HOMO energy level and the cation possesses a high LUMO energy level. In this case, the difference between the LUMO energy level of the cation and the HOMO energy level of the anion can be a good measure of the width of the electrochemical window.

Several widely used cations for preparation of ionic liquids such as pyridinium-, guanidinium-, formamidinium-, pyridazinium-, pyridinium-, imidazolium- and amidinium-based cations were selected to study the relationships between the reduction potentials and the LUMO energies of cations. The cations being considered are all similarly sized, and the differences in solvation energies are neglected, so a direct correlation between LUMO energies and reduction potentials  $\phi_{\text{red}}$  can be made. Fig.1 shows the optimized stable structure of 25 selected cations at B3LYP/6-311G\*\* level in density functional theory. The structure parameters such as bond length and angle can be obtained by requesting from the authors. The conformation energies with zero-point correction and the LUMO energies of these cations calculated from the stable structure in Fig.1 are listed in Table 1. The experiment reduction potentials of various cations are also listed in Table 1.



**Fig.1** Optimized stable structures of various cations obtained at B3LYP/6-311G\*\* level: I Pyridinium; II 1-methylpyridinium; III 1-ethylpyridinium; IV 1-propylpyridinium; V 1-butyl-pyridinium; VI 1, 3-dimethylimidazolium; VII 1-methyl-3-ethyl-imidazolium; VIII Tetramethylformamidinium; IX 1-propyl-2, 3-dimethylimidazolium; X 1-methyl-3-butyl-imidazolium; XI 1-butyl-4-(dimethylamino)pyridinium; XII 1, 2, 3-trimethylimidazolium; XIII Tetramethylammonium; XIV 1, 2-dimethylpyridinium; XV 1, 3-dimethylpyridinium; XVI 1, 4-dimethylpyridinium; XVII 1, 2, 4-trimethylpyridinium; XVIII 1, 2, 4, 6-tetramethylpyridinium; XIX 1-methylpyridazinium; XX 1-methylpyrimidinium; XXI 1-methylpyrazinium; XXII 1, 2, 3-trimethylimidazolium; XXIII Formamidinium; XXIV Guanidinium; XXV Hexamethylguanidinium

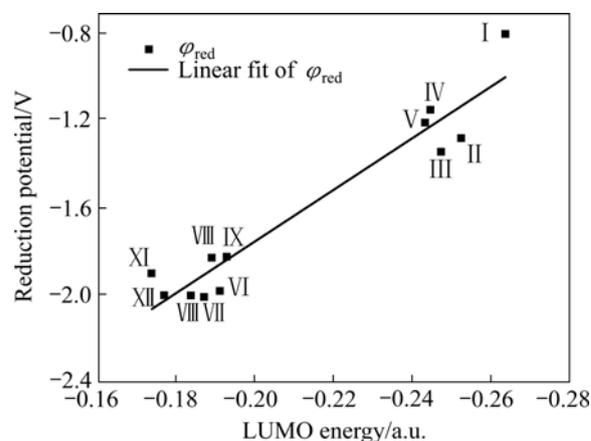
**Table 1** Conformation energies with zero-point correction and LUMO energies of 25 cations obtained at B3LYP/6-311G\*\* level

Cation No.	$E(A^+)/a.u.$	$E_{LUMO}(A^+)/a.u.$	$\varphi_{red}/V$
I	-248.603 578	-0.263 58	-0.800 [3]
II	-287.900 202	-0.252 44	-1.280 [24]
III	-327.199 194	-0.247 21	-1.340 [24]
IV	-366.494 165	-0.244 71	-1.150 [24]
V	-405.788 128	-0.243 23	-1.209 [24]
VI	-305.151 879	-0.191 25	-1.981 [24]
VII	-344.450 058	-0.187 21	-2.007 [24]
VIII	-307.512 401	-0.189 11	-1.830 [24]
IX	-423.049 099	-0.173 93	-1.900 [24]
X	-423.038 585	-0.183 97	-2.001 [24]
XI	-539.740 388	-0.192 84	-1.824 [24]
XII	-383.755 888	-0.177 16	-2.000 [24]
XIII	-327.204 072	-0.241 86	
XIV	-327.203 528	-0.244 87	
XV	-327.206 020	-0.239 90	
XVI	-366.509 345	-0.230 21	
XVII	-405.809 313	-0.222 69	
XVIII	-303.919 117	-0.278 98	
XIX	-303.940 687	-0.272 65	
XX	-303.930 670	-0.283 37	
XXI	-344.458 369	-0.181 29	
XXII	-150.347 284	-0.231 88	
XXIII	-205.724 963	-0.179 81	
XXIV	-441.4539 400	-0.167 40	
XXV	-214.0431 850	-0.149 06	

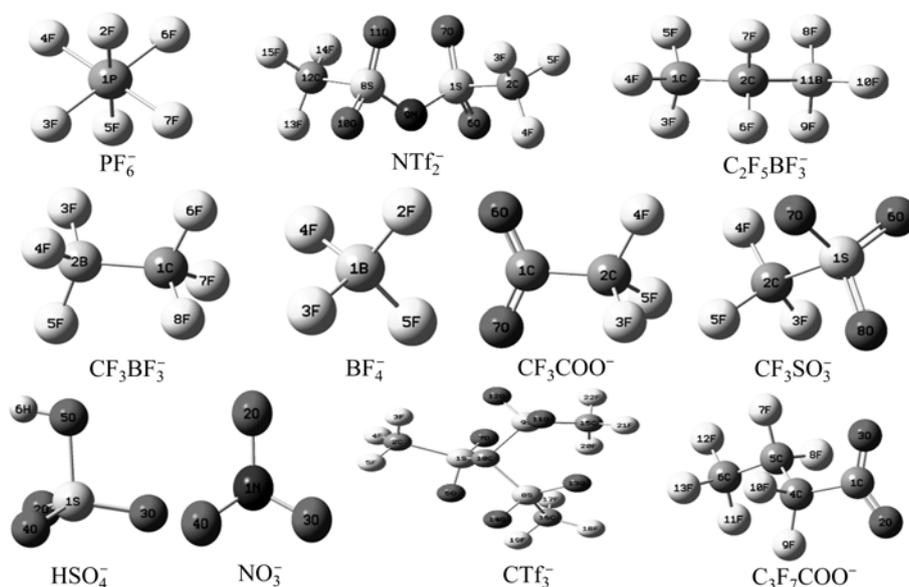
From Table 1, one can find that the aromatic 6-membered heterocycles having two ring nitrogens (XVII–XX) were predicted to be more easily reduced than the alkylpyridinium cations; thus, they were poor candidates for providing melts with a lower cathodic limit. The aromatic 5-membered heterocycles having two ring nitrogens (VII–IX, XXI) have LUMO energies significantly lower than the pyridinium based cations. The LUMO energies for the amidine (XXII, X) and guanidine (XXIII, XXIV) based cations are also low. The order of the LUMO energies for various cations is: XXV > XXIV > IX > XII > XXIII > XXI > X > VII >

VIII > VI > XI > XVII > XVI > XXII > XV > XIII > V > IV > XIV > III > II > I > XIX > XVIII > XX. As mentioned above, a low energy level of the LUMO results in a less stable cation with respect to oxidation (it is easier to put an additional electron in this orbital). Thus, one can infer that the order in electrochemical stability of these cations is 1-alkylpyrazinium < pyridinium < amidine < imidazolium < guanidinium < quaternary ammonium, which agrees well with the experimental result (pyridinium < pyrazole < phosphonium < quaternary ammonium).

Fig.2 illustrates the correlation between the calculated LUMO energies  $E_{LUMO}$  and measured reduction potentials  $\varphi_{red}$  for some anions in Table 1. It is shown in Fig.2 that a good linear correlation relationship between LUMO energies  $E_{LUMO}$  and measured reduction potentials  $\varphi_{red}$  can be found although the scatter is quite substantial and the correlation equation is given by  $\varphi_{red} (V) = -4.1385 - 11.91376 E_{LUMO} (a.u.)$  with a calculated correlation coefficient of 0.91783. It is found that the reduction potentials decrease with the increasing of LUMO energies of cations. From Table 1 and Fig.2, one can infer that the good cations for forming the ionic liquids with largest electrochemical windows may be XXV, XXIV, IX, XII, XXIII, XXII, X, VII, VIII, VI, XI, etc.

**Fig.2** Correlation of LUMO energies ( $E_{LUMO}$ ) and reduction potentials ( $\varphi_{red}$ ) of various cations

Various widely used anions for forming ionic liquids such as  $BF_4^-$ ,  $NO_3^-$ ,  $HSO_4^-$ ,  $CF_3COO^-$ ,  $CF_3SO_3^-$ ,  $C_3F_7COO^-$ ,  $NTf_2^-$ ,  $CTf_3^-$ ,  $PF_6^-$ ,  $CF_3BF_3^-$  and  $C_2F_5BF_3^-$  were selected to study the relationship between the oxidation potentials and the HOMO energies of anions. The optimized stable structures of 11 selected anions at B3LYP/6-311G\*\* level in density functional theory are given in Fig.3. The structure parameters such as bond length and angle can be obtained by requesting from the authors. Table 2 lists the conformation energies with zero-point correction, the HOMO energies of these



**Fig.3** Optimized equilibrium stable structures of various anions obtained at B3LYP/6-311G\*\* level

**Table 2** Conformation energies with zero-point correction and HOMO energies of 11 anions obtained at B3LYP/6-311G\*\* level

Anion	$E(A^-)/a.u.$	$E_{HOMO}/a.u.$	$\varphi_{\text{oxd}}/V$
$\text{BF}_4^-$	-424.581 307 0	-0.155 06	2.20 [3]
$\text{NO}_3^-$	-280.233 441 0	-0.043 68	
$\text{HSO}_4^-$	-699.528 870 0	-0.102 30	
$\text{CF}_3\text{COO}^-$	-526.254 573 0	-0.068 71	1.60 [3]
$\text{CF}_3\text{SO}_3^-$	-961.363 796 0	-0.116 09	2.30 [3]
$\text{C}_3\text{F}_7\text{COO}^-$	-1002.06 731 9	-0.068 96	
$\text{NTf}_2^-$	-1588.83 856 3	-0.143 18	2.50 [3]
$\text{CTf}_3^-$	-2696.33 564 8	-0.183 81	
$\text{PF}_6^-$	-940.649 567 0	-0.212 26	3.20 [3]
$\text{CF}_3\text{BF}_3^-$	-662.446 010 0	-0.127 96	2.32 [3]
$\text{C}_2\text{F}_5\text{BF}_3^-$	-900.289 783 0	-0.131 32	2.21 [3]

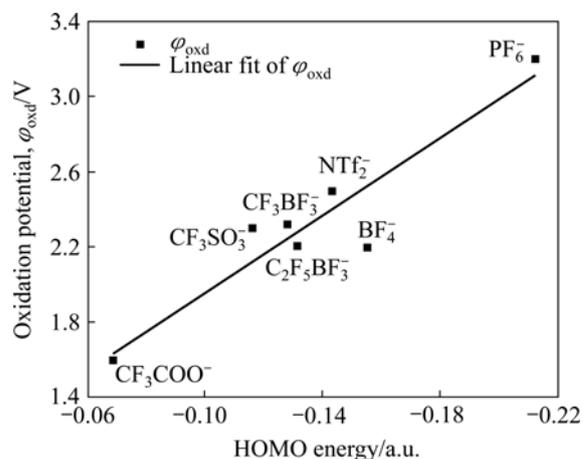
anions calculated from the stable structure, and the experiment oxidation potentials of several anions are also listed in.

From Table 2, one can find that the order of the HOMO energies for various anions is as follows:  $\text{NO}_3^- > \text{F}_3\text{COO}^- > \text{C}_3\text{F}_7\text{COO}^- > \text{HSO}_4^- > \text{CF}_3\text{SO}_3^- > \text{CF}_3\text{BF}_3^- > \text{C}_2\text{F}_5\text{BF}_3^- > \text{NTf}_2^- > \text{BF}_4^- > \text{CTf}_3^- > \text{PF}_6^-$ . As it is known that a high energy level of the highest occupied molecular orbital (HOMO) results in a less stable anion with respect to oxidation (it is easier to remove the electron from this orbital), the inferred order of electrochemical stability for anions is  $\text{NO}_3^- < \text{CF}_3\text{COO}^- < \text{C}_3\text{F}_7\text{COO}^- < \text{HSO}_4^- < \text{CF}_3\text{SO}_3^- < \text{CF}_3\text{BF}_3^- < \text{C}_2\text{F}_5\text{BF}_3^- < \text{NTf}_2^- < \text{BF}_4^- < \text{CTf}_3^- < \text{PF}_6^-$ , which agrees well with

the experimental result ( $\text{Cl}^-, \text{F}^-, \text{Br}^- < \text{AlCl}_4^-, \text{Al}_2\text{Cl}_7^- < \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^- < \text{CF}_3\text{SO}_3^-, \text{NTf}_2^-, (\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-, \text{CTf}_3^-$ ).

The calculated HOMO energies  $E_{HOMO}$  and measured oxidation potentials  $\varphi_{\text{oxd}}$  for several anions in Table 2 are shown in Fig.4. From Fig.4, one can build a reasonable linear correlation relationship between HOMO energies  $E_{HOMO}$  and measured oxidation potentials  $\varphi_{\text{oxd}}$ . The correlation equation is given by  $\varphi_{\text{oxd}}(V) = 0.932 3 - 10.270 36 E_{HOMO}(a.u.)$  with a calculated correlation coefficient of 0.897 5. It is shown that the reduction potentials increase with the decreasing of HOMO energies of cations. From Table 2 and Fig.4, one can infer that the good anions for forming the ionic liquids with largest electrochemical windows may be  $\text{CF}_3\text{SO}_3^-, \text{CF}_3\text{BF}_3^-, \text{C}_2\text{F}_5\text{BF}_3^-, \text{NTf}_2^-, \text{BF}_4^-, \text{CTf}_3^-, \text{PF}_6^-$ , etc.

In general, for a specific ionic liquid, the oxidation



**Fig.4** Correlation of HOMO energies and oxidation potentials of various anions

potential is determined by the voltage of the anion oxidation, the reduction potential is determined by the voltage of the cation reductions, and the electrochemical windows of the ionic liquid is determined by the absolute value of the difference between the oxidation potential and reduction potential. As mentioned above, the anions with higher oxidation potentials are  $\text{NTf}_2^-$ ,  $\text{BF}_4^-$ ,  $\text{CTf}_3^-$ ,  $\text{PF}_6^-$  etc. and the cations with sufficiently low reduction potentials are XXV, XXIV, IX, XII, XXIII, XXII, X, VII, VIII, VI, and XI etc. On the basis of these quantum chemical calculations, the suitable ionic liquids for electrodeposition of active metals can be inferred to be [Emim]NTf<sub>2</sub>, [Bmim]NTf<sub>2</sub>, [Bmim]BF<sub>4</sub>, [Bmim]PF<sub>6</sub>, [Bmim]CTf<sub>3</sub>, [Emim]BF<sub>4</sub>, [Emim]PF<sub>6</sub>, [Emim]CTf<sub>3</sub>, and so on.

## 4 Conclusions

1) Quantum chemical molecular orbital calculations may be used to estimate the reduction potentials of a variety of cations and the oxidation potentials of various anions. This information may be used to select promising cations and anions for the preparation of ionic liquids for electrodeposition of active metals.

2) The reasonable linear correlations between the LUMO energy and the reduction potentials for cations are obtained. The inferred order in electrochemical stability is 1-alkylpyrazinium < pyridinium < amidine < imidazolium < guanidinium < quaternary ammonium, which agrees well with the experimental result.

3) The linear relationships between the HOMO energy and the oxidation potentials of anions is found and the inferred order of electrochemical stability for anions is  $\text{NO}_3^- < \text{CF}_3\text{COO}^- < \text{C}_3\text{F}_7\text{COO}^- < \text{HSO}_4^- < \text{CF}_3\text{SO}_3^- < \text{CF}_3\text{BF}_3^- < \text{C}_2\text{F}_5\text{BF}_3^- < \text{NTf}_2^- < \text{BF}_4^- < \text{CTf}_3^- < \text{PF}_6^-$ , which agrees well with the experimental result.

4) The suitable ionic liquids with sufficiently wide electrochemical windows which are attractive candidates for electrodeposition of active metals are [Emim]NTf<sub>2</sub>, [Bmim]NTf<sub>2</sub>, [Bmim]BF<sub>4</sub>, [Bmim]PF<sub>6</sub>, [Bmim]CTf<sub>3</sub>, [Emim]BF<sub>4</sub>, [Emim]PF<sub>6</sub>, [Emim]CTf<sub>3</sub>, and so on.

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