Calculations of silicon complexes in KF–KCl–KI–K$_2$SiF$_6$ and KF–KCl–KI–K$_2$SiF$_6$–SiO$_2$ molten electrolytes

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Calculations of Silicon Complexes in KF–KCl–KI–K$_2$SiF$_6$ and KF–KCl–KI–K$_2$SiF$_6$–SiO$_2$ Molten Electrolytes

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Abstract. The stability of silicon complexes formed in KF-KI-KCl-K$_2$SiF$_6$ and KF-KCl-KI-K$_2$SiF$_6$-SiO$_2$ was studied using the density functional theory method. The calculations of the bond energy Si-F and Si-I were performed. Conclusions about the stability of silicon complexes containing different amounts of iodine ions in the inner coordination sphere were made. All oxyfluoride silicate complex compounds became extremely unstable when replacing fluoride with iodide ion.

INTRODUCTION

Silicon-based materials offer new opportunities for improving the efficiency of lithium-ion batteries and devices used in solar energy [1]. Anodic silicon materials have a high capacity of 4200 mA·h/g, which is associated with the formation of lithium silicide according to the following scheme: $4.4Li^+ + Si + 4.4\bar{e} \leftrightarrow Li_{4.4}Si$ [2, 3]. Graphite materials are analogous to silicon, they are well studied and are actively used, but have a capacity is over 8 times less, about 550 mA·h/g, because the introduction of lithium ions occurs with the participation of one electron – $6C + Li^+ + \bar{e} \leftrightarrow LiC_6$ [4]. Based on these data, it can be argued that thin silicon films will reduce the material consumption of photovoltaic cells [5, 6].

Materials of various forms, nanofibres, thin films and coatings, can be obtained by the method of electrolysis from ionic melts of alkali metal halides based on KF–KCl containing K$_2$SiF$_6$ and SiO$_2$ [7-9]. Since molten salts are aggressive media, their use requires careful selection of structural materials. The specific properties of environments require the development of model approaches for their study. Experimental study of the structure of complex compounds to explain the processes occurring in molten salts is a difficult problem [10-12].

Recently, significant advances have been made in this area – silicon films were synthesized in the KF–KCl–K$_2$SiF$_6$ melt; the photoelectric conductivity of silicon films was confirmed, and complexes of various compositions were obtained [13–15].

In this work two melts were considered – KF–KCl–KI–K$_2$SiF$_6$ and KF–KCl–KI–K$_2$SiF$_6$-SiO$_2$, and the resulting complexes, their stability was analyzed depending on the composition of the electrolyte and the morphology of the cathode deposits is studied.

The structure of the complexes can be reliably enough calculated using the density functional theory (DFT). The calculations made in [16] were in good agreement with the experimental data. Based on the data obtained on the basis of the density functional theory, the influence of the elemental composition of anions and cations from the coordination sphere on the binding energy of complex anions can be deduced, as well as the change in bond energy when replacing cations or anions in a complex, and their effect on stability of the entire complex.

The purpose of this work was to identify the effect of potassium iodide in the melt on the structure of the formed silicon-based fluoride and oxyfluoride complexes and their stability. The obtained data will help to interpret the patterns of changes in the physicochemical properties of the melt on the final morphology of cathode deposits based

on silicon. In [17] it was shown that an increase in the concentration of potassium iodide in the melt leads to the formation of more compact silicon precipitates.

MODEL

Using the density functional theory method we studied the stability of silicon complexes formed in KF–KCl–KI–K_2SiF_6 and KF–KCl–KI–K_2SiF_6-SiO_2 systems Siesta software package has been selected for the simulation [18]. The calculations were performed both for iodide-fluoride silicon complexes, and for oxyfluorodiodic ones. Geometric optimization using a generalized gradient approximation in the form of PBE was performed for all the considered complexes. Dynamic relaxation of atoms was carried out until the change in the total energy of the system was less than 0.001 eV. The energy for cutting the basis of plane waves was assumed to be 300 Ry.

Binding energies in silicon complexes were calculated by the formula:

$$\tag{1}$$

where E_{total}, E_{Si}, E_F and E_I are the total energy of the complex, a single silicon ion (Si^{4+}), fluorine (F^-) and iodine (I^-), respectively, and N_{Si}, N_F, N_I is the number of silicon ions, fluorine and oxygen in the system.

RESULTS AND DISCUSSION

We performed DFT calculations of the binding energy for silicon complexes of various structures that can be formed in KF–KCl–KI–K_2SiF_6 and KF–KCl–KI–K_2SiF_6-SiO_2 melts. It was established that all combinations of oxyfluoride complex compounds decompose when fluoride is replaced by iodide ions.

The following iodide-fluoride complex groups were considered: $[SiX_4]$, $[SiX_5]^-$, $[SiX_6]^{2-}$, and $[SiX_7]^{3-}$, where X are fluorine and iodine atoms. All the considered oxyfluoride complex compounds and $[SiX_7]^{3-}$ complex groups collapsed when fluorine was replaced by iodine ions. The results of calculations of the binding energies of Si^{4+} cations in silicon complexes are presented in Table 1. It is seen that with the gradual replacement of fluorine by iodine, an increase in the binding energy occurs, i.e. a loss of stability of the complex compounds occurs. The most stable iodine complex compound is $[SiF_4I]^-$ with binding energy of –110.94 eV.

The average bond lengths for these compounds are shown in Table 2. Based on the data obtained, several conclusions can be drawn. First, the length of the Si–I bond is greater than that of Si–F bond, and as the content of iodine atoms in the complex compound increases, both the average Si–I bond length and the Si–F bond length increase.

TABLE 1. Binding energies (eV) in fluoride complex compounds depending on the content of iodine ions, where X is F and I.

Complex Compound	Number of I^- Ions in the Complex Compound						
	0	1	2	3	4	5	6
$[SiX_4]$	–109.68	–106.34	–102.97	–99.61	–96.29	–	–
$[SiX_5]^-$	–112.76	–110.94	–107.60	–104.09	–100.75	–97.13	–
$[SiX_6]^{2-}$	–113.19	$[SiF_5]^- + I^-$	–107.68	–104.48	–101.48	–98.09	–94.69

TABLE 2. Average bond lengths (Å) of Si–F and Si–I in fluoride complex compounds depending on the content of iodine ions, where X is F and I.

Bond	Complex Compound	Number of I^- Ions in the Complex Compound						
		0	1	2	3	4	5	6
Si–F	$[SiX_4]$	–	2.421	2.442	2.460	2.479	–	–
	$[SiX_5]^-$	–	2.641	2.594	2.547	2.568	2.547	–
	$[SiX_6]^{2-}$	–	$[SiF_5]^- + I^-$	2.916	2.824	2.759	2.747	2.742
Si–I	$[SiX_4]$	1.615	1.627	1.642	1.655	–	–	–
	$[SiX_5]^-$	1.666	1.672	1.677	1.691	1.712	–	–
	$[SiX_6]^{2-}$	1.757	$[SiF_5]^- + I^-$	1.692	1.701	1.699	1.707	–

Therefore, complex compounds containing iodine always have a larger size than fluoride compounds, as can be seen from the comparison of Figs. 1(a) and 1(b). Thirdly, the replacement of one F^- ion in the $[SiF_6]^{2-}$ compound

with an iodine ion I$^-$ leads to the decomposition of this compound into the [SiF$_5$]$^-$ fluoride complex and the I$^-$ iodine ion (Fig. 2).

(a)　　　　　　　　　　　　　　　　　　(b)
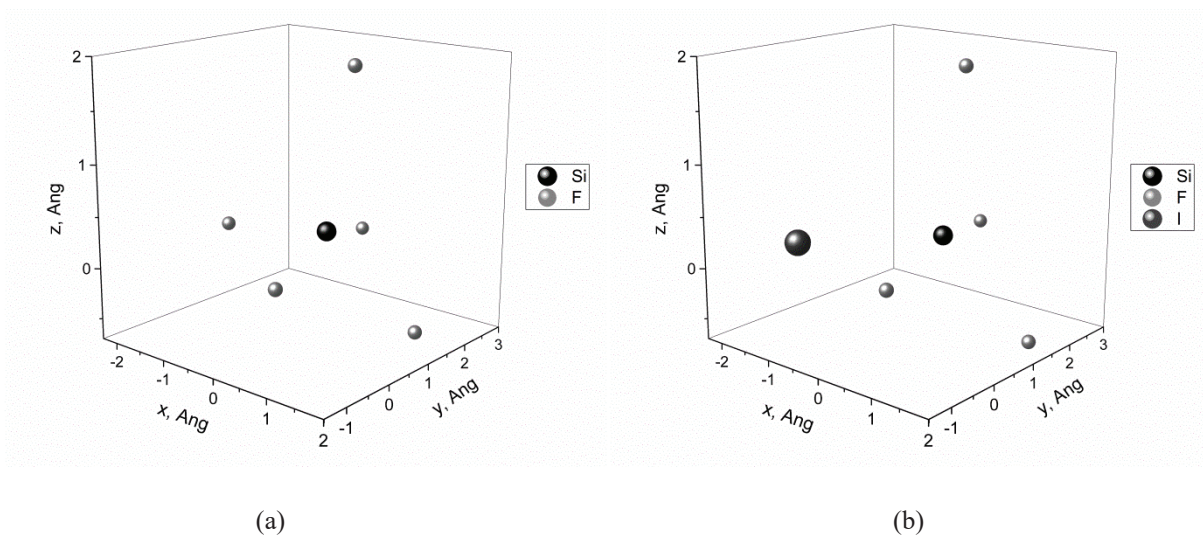
FIGURE 1. Results of geometry structures calculations of silicon complexes (a) [SiF$_5$]$^-$ and (b) [SiF$_4$I]$^-$
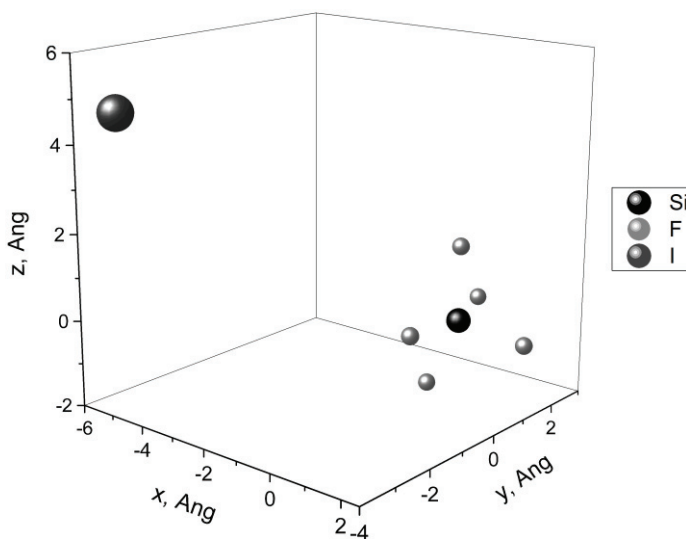
FIGURE 2. Results of geometry structures calculations of silicon complex [SiF$_5$I]$^{2-}$

CONCLUSIONS

All the considered iodide–fluoride complex groups [SiX$_4$], [SiX$_5$]$^-$, [SiX$_6$]$^{2-}$ and [SiX$_7$]$^{3-}$ have comparable binding energies. The addition of KI to the melt leads to an increase in the Si–F bond energy, and consequently to a decrease in the stability of the complex and a decrease in electrical conductivity. All oxyfluoride complex compounds decompose when fluorine is replaced by iodine ions.

The most stable iodine complex compound is [SiF$_4$I]$^-$ with binding energy of –110.94 eV but the oxidation state of silicon in it does not correspond to literature experimental data.

The lengths and binding energies of complex silicon anions containing Si–F, Si–I bonds formed in the KF–KCl–KI–K_2SiF_6 melts are calculated. It is established that the most stable remains the complex SiF_6^{2-}. It is shown that the gradual replacement of fluorine by iodine in the complexes leads to a loss of stability of the complex. However, the binding energies in the SiF_6^{2-} and $SiI_2F_4^{2-}$ complexes are comparable and amount to –113.19 eV and –107.68 eV, respectively.

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