

**РЕЗЮМЕ.** Новый метод синтеза наноразмерных металлов Fe, Co и Ni в коллоидной форме и в виде нанопорошков основан на восстановлении галогенидов металлов нафталидом натрия в растворах N-метилпирролидона (НМП). Реакции при комнатной температуре сопровождаются нагреванием раствора до 170–200 °С в результате образования наночастиц металлического железа и кобальта, а также карбида никеля Ni<sub>3</sub>C. Коллоидный металлический никель получен по реакции коллоидного железа с NiCl<sub>2</sub> в растворах НМП. Поверхность металлических наночастиц восприимчива к химическому замещению; в результате постсинтетических реакций этих частиц с олеиновой кислотой получены продукты, растворимые в углеводородах.

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## FTIR-SPECTROSCOPIC STUDIES OF TANTALUM (V) SPECIES FORMED IN 1-BUTYL-1-METHYL-PYRROLIDINIUM CHLORIDE—TaCl<sub>5</sub> IONIC LIQUID WITH ADDITIVES OF ALKALI HALIDES

Ionic liquid 1-butyl-1-methyl-1-pyrrolidinium chloride—TaCl<sub>5</sub> (molar ratio 65:35) was synthesized with the aim of electrochemical deposition of tantalum coatings at ambient temperature. To elucidate the mechanism of the deposition process, FTIR spectroscopic studies were performed. A detailed analysis indicates the formation of TaCl<sub>6</sub><sup>-</sup> complexes and some oxochloride complexes of tantalum (V) with bridge oxygen bonds Ta—O—Ta. Addition of alkali chlorides has no effect on the vibrational features of tantalum (V), whereas LiF leads to the formation of mixed complexes TaCl<sub>6-n</sub>F<sub>n</sub><sup>-</sup> with simultaneously decreasing amount of the tantalum (V) species with Ta—O—Ta bridge bonds.

Low-temperature molten salts (LTMS), or ionic liquids, which are a combination of organic and inorganic compounds, are very attractive and promising media for electrochemical deposition of highly reactive metals, such as refractory metals that cannot be obtained from aqueous solutions or only out of high-temperature molten salts. One of the important advantages of the deposition from ionic liquids is that the properties of the substrates are not changed during electrochemical treatment as in the case of high-temperature molten salts.

A few studies concerning attempts of electrodeposition of tantalum (V) from ionic liquids were published: the electrodeposition of tantalum from EMIC—AlCl<sub>3</sub> was studied by Barnard and Hussey [1], from EMIC — by Matsunaga [2]. Only the first steps corresponding to Ta<sup>5+</sup>/Ta<sup>2+</sup> reactions were discussed. The electrodeposition of tantalum metal was not achieved. The addition of LiF to EMIC—TaCl<sub>5</sub> leads to the electrodeposition of tantalum, which was reported by Morimitsu and Matsunaga [3].

The influence of alkali metal cations on the elect-

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rodeposition of tantalum from high-temperature molten salts is well known. The most successful attempt of the deposition of tantalum coatings performed by Mellors and Senderoff [4] was achieved only in the presence of  $K^+$  cations.

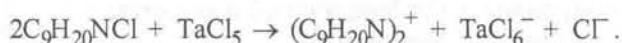
Motivated by the lack of FTIR-spectroscopic data on tantalum chlorides and oxochlorides in ionic liquids and by the possibility to obtain electrochemically tantalum coatings on various substrates in the presence of LiF, we have performed spectroscopic studies of electrochemically active species of tantalum (V) in the novel ionic liquid 1-butyl-1-methyl-pyrrolidinium chloride— $TaCl_5$  with additives of alkali halides, which has promising properties as electrolyte for electrochemical deposition of tantalum coatings.

**Synthesis.** Stirring of the mixture of 1-butyl-1-methyl pyrrolidinium chloride (BMPC) with  $TaCl_5$  at the molar ratio 65:35 leads to the formation of a liquid at temperatures above 80 °C. The synthesis was performed in a Pyrex tube in inert atmosphere of argon (99.999) placed in an oil bath. The handling of the samples was done in a glove box MBRAUN Star containing <1 ppm oxygen and moisture. The ionic liquid BMPC— $TaCl_5$  is stable in the temperature range 80—180 °C. Compositions with 10 mol. % of alkali chlorides (LiCl, NaCl, KCl, RbCl, CsCl) were prepared. The influence of LiCl and LiF was investigated at the concentrations 3.5 and 10 mol. %.

**Chemicals.** 1-Butyl-1-methyl pyrrolidinium chloride (BMPC) (Merck, moisture content <100 ppm) is a white powder with a melting point of 203 °C, decomposing at 210 °C. It was preliminarily dried in high vacuum (up to 0.013 mbar) at 80—100 °C with stirring during 48 h.  $TaCl_5$  (Alpha Aesar 99.99 %) was used without preliminary purification. Alkali chlorides and LiF p.a. quality from Merck were dried for at least 24 h at 150 °C under high vacuum and purified by melt recrystallization in inert atmosphere. Only transparent pieces were used for experiments.

**Spectroscopic measurements.** FTIR internal reflection (Golden Gate ATR unit with KRS5 lince) spectroscopic technique was used for the determination of the structure and composition of electrochemically active species of tantalum (V) in ionic liquid BMPC— $TaCl_5$ . FTIR spectra were recorded using a Bruker FTIR spectrometer Equinox 55 with a MCT nitrogen cooled detector in the range 4000—250  $cm^{-1}$ .

**BMPC— $TaCl_5$ .** The formation of ionic liquid BMPC— $TaCl_5$  at the molar ratio 65:35 occurs according to the reaction:



The main species present in BMPC— $TaCl_5$  are complex anions  $TaCl_6^-$ . At a  $TaCl_5$  concentration of 35 mol. % of one can expect the formation of a quasi crystal lattice with  $[TaCl_6]$  structural unit and

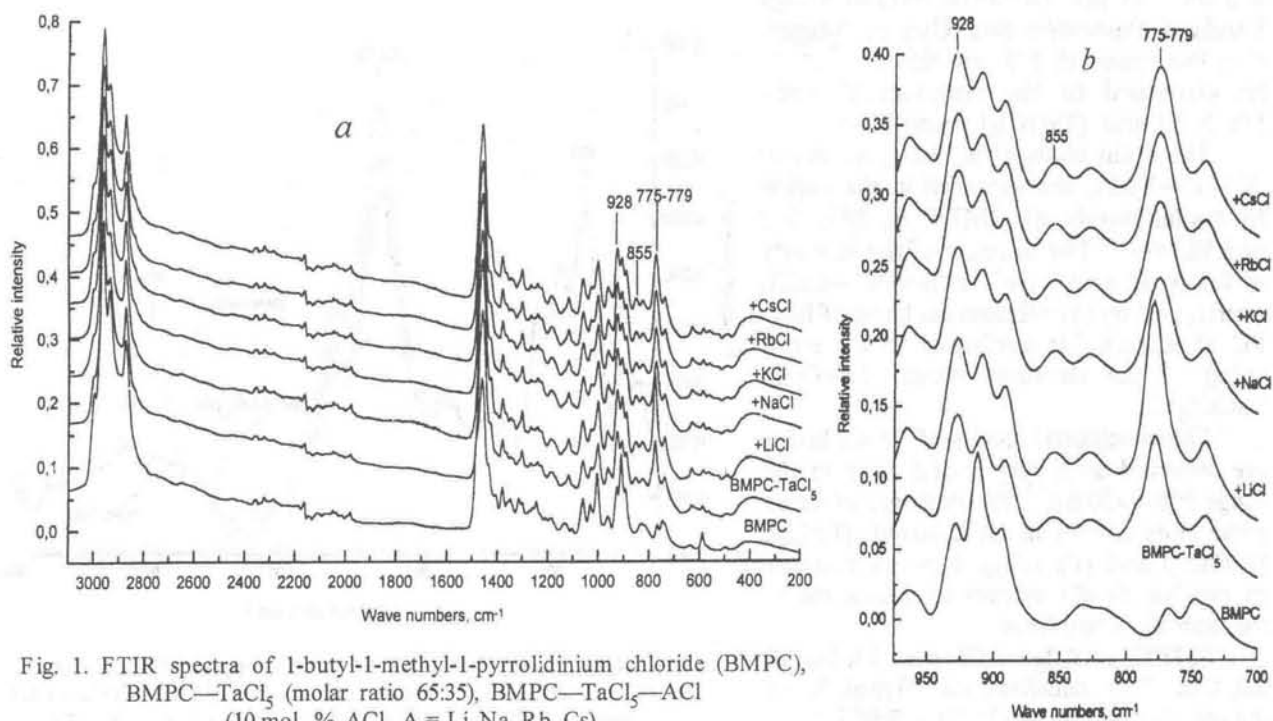


Fig. 1. FTIR spectra of 1-butyl-1-methyl-1-pyrrolidinium chloride (BMPC), BMPC— $TaCl_5$  (molar ratio 65:35), BMPC— $TaCl_5$ — $ACl$  (10 mol. %  $ACl$ ,  $A = Li, Na, Rb, Cs$ ).

oligomeric complexes of tantalum (V). Because of the strong ability of refractory metals to form oxochloride complexes one has to take into consideration also the formation of the oxochloride complexes of tantalum (V).

FTIR spectra of BMPC, BMPC—TaCl<sub>5</sub> and BMPC—TaCl<sub>5</sub> with additives of alkali chlorides (10 mol. %) are presented in fig. 1. Comparison of the FTIR spectra of BMPC and BMPC—TaCl<sub>5</sub> shows that introduction of 35 mol. % TaCl<sub>5</sub> into BMPC does not cause significant changes into the vibrational features of BMPC in the range 4000—1000 cm<sup>-1</sup> (fig. 1, a). Therefore our attention is concentrated in the range of the vibrations of tantalum (V) species, 1000—250 cm<sup>-1</sup>, where the main changes are observed (fig. 1, b).

The FTIR spectrum of BMPC—TaCl<sub>5</sub> is characterized by a new vibrational feature at 778 (vs), 855 (w) and 928 (m) cm<sup>-1</sup>. Because of the strong ability of refractory metals to form oxochloride complexes one can suggest that the origin of these vibrational bands is the formation of oxochloride complexes of tantalum (V).

Ta—O—Ta oxygen bridge bonds typically show vibrational bands in the region 700—850 cm<sup>-1</sup> [5, 6]. It seems reasonable to assign the vibrational bands at 778 and 855 cm<sup>-1</sup> to the Ta—O—Ta oxygen bridge bonds in oligomeric ions. One can suggest that the bands at 778 and 855 cm<sup>-1</sup> could be attributed to the tantalum (V) units [TaOCl<sub>5</sub>] and [TaOCl<sub>4</sub>] respectively.

The main changes in the spectrum of BMPC—TaCl<sub>5</sub> are observed in the region of triplet bands of BMPC at 892, 910 and 927 cm<sup>-1</sup>. The increase of the intensity of the band at 928 cm<sup>-1</sup> in BMPC—TaCl<sub>5</sub> overlapped by the vibrational band of BMPC at 927 cm<sup>-1</sup> is attributed to the stretching of the terminal oxygen Ta=O in TaOCl<sub>5</sub><sup>2-</sup>.

The vibrational modes of Ta—Cl bonds are observed as a very broad band in the range 300—450 cm<sup>-1</sup>. Because several structural units coexist in ionic liquid, [TaCl<sub>6</sub>], [TaOCl<sub>5</sub>] and [TaOCl<sub>4</sub>], it is not possible to resolve Ta—Cl vibrations belonging to the specific complexes.

BMPC—TaCl<sub>5</sub>—ACl (A — Li, Na, K, Rb, Cs). The additives of 10 mol. % of the alkali chlorides NaCl, KCl, RbCl, CsCl

do not cause crucial changes in FTIR spectra of BMPC—TaCl<sub>5</sub> (fig. 1, a, b) except for the slight shift of the vibration from 778 to 775 cm<sup>-1</sup> and insignificant increase of the intensity of the vibrations at 778 cm<sup>-1</sup> from Na<sup>+</sup> to Cs<sup>+</sup>.

Addition of LiCl (10 mol. %) causes an increase of the intensity of the vibration 778 cm<sup>-1</sup> and a shift to 779 cm<sup>-1</sup>, and this is the only change in comparison with those with the addition of other alkali chlorides.

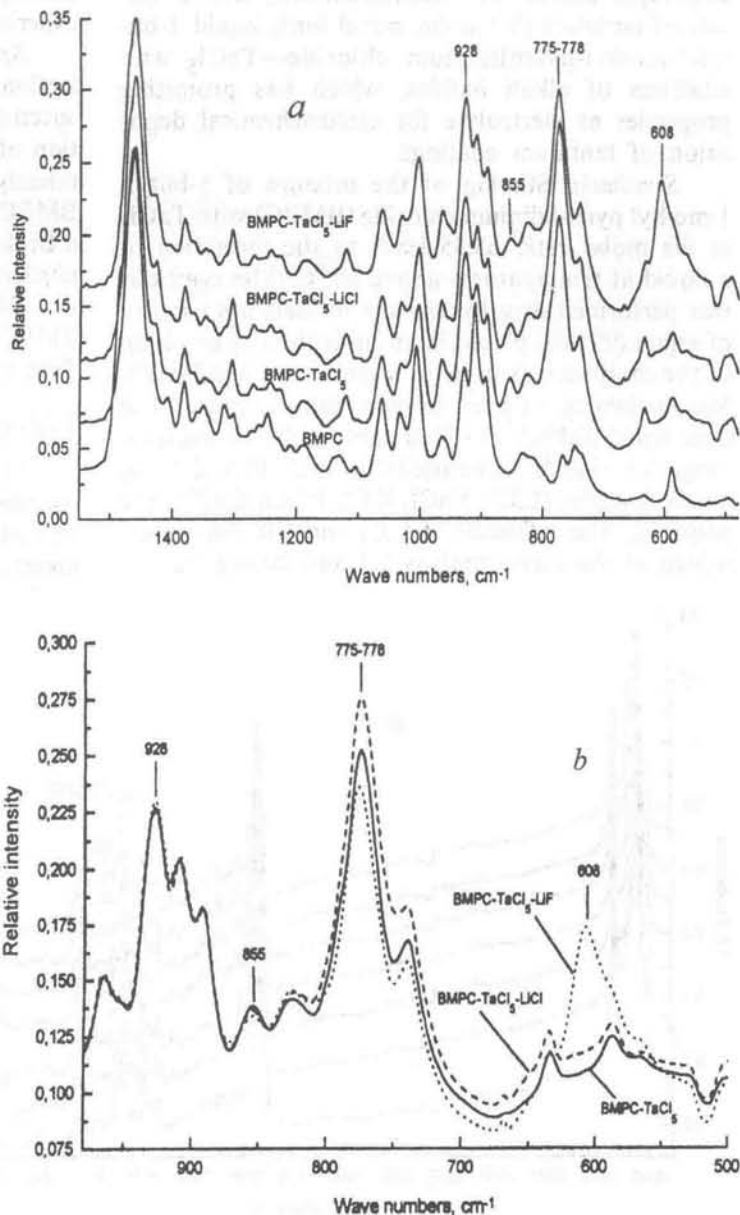


Fig. 2. FTIR spectra of 1-butyl-1-methyl-1-pyrrolidinium chloride (BMPC), BMPC—TaCl<sub>5</sub> (molar ratio 65:35), BMPC—TaCl<sub>5</sub>—LiCl (10 mol. % LiCl) and BMPC—TaCl<sub>5</sub>—LiF (10 mol. % LiF).

**BMPC—TaCl<sub>5</sub>—LiCl and BMPC—TaCl<sub>5</sub>—LiF.** FTIR spectra of BMPC—TaCl<sub>5</sub> (molar ratio 65:35) with the additives of 10 mol. % LiCl and LiF are presented in fig. 2, *a*, detailed spectra in fig. 2, *b*.

Three bands at 928, 910 and 892 cm<sup>-1</sup> of BMPC—TaCl<sub>5</sub> do not change under the influence of the additives of LiCl or LiF. The addition of LiCl leads to a very slight decrease of the intensity of the band at 855 cm<sup>-1</sup> and increase of the intensity of the band at 775 cm<sup>-1</sup>. This indicates an increase of the amount of the species with Ta—O—Ta bridge bonds.

A new vibrational feature at 608 cm<sup>-1</sup> appears in the spectrum of BMPC—TaCl<sub>5</sub>—LiF. The addition of LiF results in insignificant decrease of the intensity of the band at 855 cm<sup>-1</sup>, but strong decrease of the intensity of the band at 775 cm<sup>-1</sup> (contrary to LiCl) and its shift to 777 cm<sup>-1</sup>. Agulyanskii [7] had investigated the equilibrium TaF<sub>6</sub><sup>-</sup> ↔ TaF<sub>7</sub><sup>2-</sup> in alkali metal fluoride melts using IR emission spectroscopy. The vibrations of TaF<sub>6</sub><sup>-</sup> complex have been found in the range 607—593 cm<sup>-1</sup> and those of TaF<sub>7</sub><sup>2-</sup> in the range 542—516 cm<sup>-1</sup> depending on alkali cations. The new vibrational mode 608 cm<sup>-1</sup> is assigned to the stretching vibration Ta—F in the structural unit [TaCl<sub>6-n</sub>F<sub>n</sub>]. The formation of the mixed complex TaCl<sub>6-n</sub>F<sub>n</sub> seems more probable than that of TaF<sub>6</sub><sup>-</sup> because of the low concentration of LiF (10 mol. %). On the basis of FTIR spectra one can observe that the addition of LiF leads to a decrease of the amount of the tantalum (V) species with Ta—O—Ta bridge bonds and formation of mixed chloro-fluoride complexes.

The infrared vibrational frequencies of tantalum species are presented in the table.

FTIR spectra of ionic liquid 1-butyl-1-methyl-pyrrolidinium chloride—TaCl<sub>5</sub> (molar ratio 65:35) indicate the formation of TaCl<sub>6</sub><sup>-</sup> complexes and some oxochloride complexes of tantalum with bridge oxygen bridge bonds Ta—O—Ta. Additives of alkali chlorides do not cause changes in the vibrational features of tantalum (V). In the presence of LiF the formation of mixed complexes TaCl<sub>6-n</sub>F<sub>n</sub> is observed with simultaneously decreasing amount of the

**Vibrational frequencies of tantalum species in BMPC—TaCl<sub>5</sub> ionic liquid with the additives LiCl and LiF**

BMPC— TaCl <sub>5</sub>	BMPC— TaCl <sub>5</sub> —LiCl	BMPC— TaCl <sub>5</sub> —LiF	Vibrational bonds
928	928	928	Ta=O
855	855	854	Ta—O—Ta
755	775	776	Ta—O—Ta
		608	Ta—F
300—450	300—450	300—450	Ta—Cl

tantalum (V) species with Ta—O—Ta bridge bonds.

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**РЕЗЮМЕ.** Синтезирована ионная жидкость 1-бутил-1-метил-1-пирролидиний хлорид—TaCl<sub>5</sub> (мольное соотношение 65:35) с целью электрохимического осаждения танталовых покрытий при температуре окружающей среды. Методом ИК-спектроскопии с Фурье-преобразованием исследован механизм осаждения. Установлено образование комплексов TaCl<sub>6</sub><sup>-</sup> и некоторых оксохлоридных комплексов Ta (V) с мостиковыми кислородными связями Ta—O—Ta.

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