

Diamond Electrodes in Molten Salts: Theory, Experiment, Application

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During the last 10 years, diamond as a new electrode material attracts great attention of electrochemists because of its extraordinary chemical and physical stability. Extensive researches have been done to investigate structural, chemical peculiarities and the electrochemical behavior of various types of diamond and diamond-like electrodes (semiconductive films and single crystals) in different electrode reactions in aqueous and organic electrolytes [1,2,3].

Electrochemical behavior of diamond electrodes in molten salts have not been studied because of difficulties in electrode forming at high temperature (electrode construction, ohmic contact). Electrochemical studies of diamond in our institute have been begun over 15 years ago. It was found that dielectric synthetic and natural diamond single crystals when in contact with ionic melts of certain chemical composition take on the property to conduct electric current. The study of interaction which takes place on diamond – ionic melt interface was carried out for finding the reason of conductivity appearance in diamond.

The experiments in the forming of diamond electrodes and the values of its volume resistance showed that conductivity was realized on the diamond surface.

Diamond electrode represented a container made of platinum net and filled with natural (2-3 mm) or synthetic diamond single crystals of 400/315; 315/250; 160/125 μm fineness. The current lead to the container was a platinum wire. We call this electrode as combined diamond-platinum electrode.

The conception of surface conductivity which is the result of red-ox processes taking place at the diamond – ionic melt interface is proposed for explaining this phenomenon. We have carried out a thermodynamic analysis of diamond possible reaction with oxide compounds of IV – VI group elements. The Free Gibbs energy of the most probable reactions of diamond oxidation was calculated at the temperature 900 – 1200 K. Calculations have shown that Na_2WO_4 ; Na_2MoO_4 ; $\text{Na}_2\text{W}_2\text{O}_7$; $\text{Na}_2\text{Mo}_2\text{O}_7$; CO_2 – are the most suitable oxidants for the realization of diamond electrode function in molten salts ($\Delta G^0_{1000} \leq -50 \text{ kJ mol}^{-1}$).

The influence of diamond different types treatment by various melts at 1000 K

- (1) Equimolar mixture $\text{NaCl} - \text{KCl}$;
- (2) Equimolar mixture $\text{NaCl} - \text{KCl} - \text{CO}_2$ (pressure);
- (3) Na_2WO_4 ;
- (4) $\text{Na}_2\text{WO}_4 - x \text{WO}_3$ (MoO_3)

on the diamond surface structural peculiarities was investigated by the methods of X – ray emission and EPR spectroscopy. It was found by EPR method that there was no conductive metallic film on diamond surface after 3 – hours diamond standing in the above melts without current load. X –ray emission spectroscopy showed that molten treatment results to break of bonds of carbon surface atoms with other element atoms adsorbed from environment during the diamond synthesis and the recombination of C – C bond takes place. It may leads to diamond surface reconstruction and the filling of diamond surface states. According to the results of calculation of the electronic structure of diamond (111) surfaces [4] using a self- consistent pseudopotential method an

interesting conclusion was made by the authors: the ideal diamond surface is metallic.

The potentiometric and voltammetric investigations at diamond-combined electrodes were carried out in the above mentioned melts [5]. It was found that in pure chloride melt the diamond has no own potential (its value is equal to platinum potential). The potential of diamond, more negative than platinum potential is fixed in chloride – oxide ($\text{NaCl} - \text{KCl} - \text{CO}_2$ (Na_2WO_4 ; Na_2MoO_4) and oxide melts ($\text{Na}_2\text{WO}_4 - x\text{WO}_3$ (MoO_3)). The diamond electrode potential responds to changes in the acid – base properties of the melts.

In the voltammetric study a considerable increase of electroreduction currents of CO_2 ; $\text{Mo}_2\text{O}_7^{2-}$; $\text{W}_2\text{O}_7^{2-}$ on diamond electrode as against platinum container is fixed. This fact can be explained by increasing in diamond working electrode area, which becomes possible due to the origination of diamond surface conduction. We determined CO_2 reduction currents on the diamond surface by subtracting the current on the platinum net from the total combined diamond – platinum electrode current. Using the data reported in [6,7] we calculated the diamond active area to be 25 cm^2 . The value obtained is in good agreement with the surface area of diamond of given fineness calculated from handbook data [8].

The results obtained make it possible to use in a more goal-directed way the diamond surface conduction phenomenon for the two main applied purposes.

The first – for plating diamonds by melt electrolysis, e.g. the direct diamond metallization from molten salts by refractory metals and their carbides. The second – for the high temperature electrochemical synthesis of diamond and diamond-like films on diamond. This synthesis is based on the realization of carbon dioxide reduction to carbon on the conductive diamond surface.

This research has been partly supported by the STCU project 1622

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