3. Electrochemistry of Glass-Forming Melts

3.1 Introduction

Friedrich G.K. Baucke

This chapter is concerned with the electrochemistry of oxidic glass-forming melts, and it may be mentioned at the outset that, in a strict sense, the term glass-forming melts is a more accurate name for this class of materials than just glass melts, at least with regard to glass production, because they are produced to become, but have never before been, glasses. Because, however, both terms are frequently used also for glasses that have been remelted, for instance in laboratories, melts treated in this chapter will not only be called glass-forming melts but will occasionally be termed glass melts.

Unlike solid glasses, oxidic glass-forming melts are good electrolytes. Despite their usually high viscosities, their ionic conductivity at temperatures of about 800–1600°C, which are of interest here, is comparable to that of aqueous salt solutions at environmental temperatures. Glass-forming melts are highly reactive, not only chemically but also electrochemically, because kinetic hindrances of electrode reactions are mostly excluded at the high temperatures. Moreover, glass melts are characterized by a reduction-oxidation or, briefly, redox state caused by dissolved oxygen and by differently charged ions of polyvalent oxides, which are generally dissolved in the melt. They form so-called redox equilibria, which make the melts more or less oxidizing or reducing materials.

These properties, inter alia, make glass-forming melts ideal media for electrochemical research and its application in technical glass melting. Thus, crucibles and containers for batch-wise production, which contain up to tens of tonnes of melt, as well as continuously working tanks, which produce up to several hundred tonnes of glass per day, must actually be viewed as large electrochemical cells. On the one hand, the various electrochemical processes proceeding in these cells are required as a part of the melting process; but on the other hand they are intolerable reactions which are caused by certain parameters of the melting tanks and disturb the production process and impair the quality of the glass product. Some examples may demonstrate the variety of electrochemical reactions. The melts are often subject to alternating currents of up to hundreds of kA for direct electric heating, their redox state...
is changed between the extremes of the equilibria by strong temperature variations, which are to generate millions of oxygen bubbles for fining the melt, electrolytic cells unintentionally set up by metal parts of the tanks and driven by stray voltages tend to electrolyse the melts, and concentration and thermoelectric cells formed with electron conductors would immediately cause deleterious reactions on short-circuiting. In addition, the refractories of the containers are frequently corroded electrochemically, and the electrodes supplying the electric energy for heating are subject to corrosion as a direct or sometimes indirect consequence of the high current densities of up to several hundred amperes per square centimetre.

In view of this situation, the electrochemical research done in the field of glass melts by the Electrochemical Laboratory of Schott Glas has necessarily been practice- and production-oriented. We endeavoured to deepen our understanding of the electrochemical phenomena with the ultimate goal of improving the economy and ecology of the melting process as well as the glass quality on the basis of a better understanding of the electrochemical phenomena. The electrochemical characterization of oxidic glass-forming melts given in Sect. 3.2 provides a base for understanding the information given in the following. Section 3.3 is on the basicity of glasses. It is concerned with “oxide”, the reduced compound of the intrinsic redox couple “oxide"/oxygen of oxidic melts, the development of basicity concepts and especially on the meaning of optical basicity and its application to redox reactions in melts. This section was written by one of the workers who developed optical basicity. Section 3.4 is on oxygen in glass-forming melts, which represents the oxidized counterpart of “oxide”. It is directly connected to the production at Schott Glas, as it reports on the development of oxygen sensors for laboratory and technical application. It also describes how basic problems of the platinum measuring and the zirconia reference electrodes have been solved and how the thermodynamically correct functioning of the sensors was verified. Principle and application of alternative (metal) reference electrodes, which are mechanically more stable but electrochemically more demanding than zirconia electrodes, will also be described.

Section 3.5 is concerned with the application of oxygen sensors to control fining of glass-forming melts. It starts with a description of fining in general and redox fining in particular, including basic information about sulphur fining, which, although not practically applied at Schott Glas, is the most frequently applied fining process and is used for nearly all mass-produced glasses world-wide. Also reported is the determination of thermodynamic standard data of polyvalent elements dissolved in glass melts by indirect and in situ methods, which are increasingly needed for an improved evaluation of oxygen partial pressures measured in technical melting units. Subsequently, a comparative test of Schott sensors with sensors of different design and origin in a large-scale technical melter is reported. Finally we propose an alternative fining procedure, called electrolytic fining, which is based on electrolytically