Battery effect in 'electric current arising from unpolarized polyvinyl formal'

ASHOK K VIJH

Institut de recherche d'Hydro-Québec, 1800 Lionel-Boulet, Varennes, (Qc), Canada J3X 1S1

Abstract. Thermally-stimulated currents (TSC) observed in metal–(insulating polymer)–metal systems are shown to be of electrochemical origin, owing to the battery configuration of these devices.

Keywords. TSC; battery effect; metal–polymer–metal devices.

1. Introduction

Khare *et al* (2000) have recently reported some interesting data obtained on polyvinyl formal (PVF) sandwiched between two metal electrodes; on heating in the temperature range 30–110°C, an appreciable electric current is observed which is usually called thermally-stimulated current (TSC). Many authors (Ieda *et al* 1975; Pillai *et al* 1979; Khare *et al* 2000) have used this technique ostensibly for obtaining information on trapped charges and dipole relaxation processes in polymeric materials. Most of the interpretations are usually attempted in terms of work functions of the metals and the contact potentials at metal–polymer interfaces, as Khare *et al* (2000) have indeed done, without taking into account the electrochemical reaction that occur at the metal–polymer interfaces owing to the presence of H_3O^+, OH^-, organic groups such as –R–OH, and residues of polymerizing catalysts and other impurities in the polymer. The author has previously shown (Vijh 1978, 1979, 1986) that for a large number of metal–polymer–metal sandwiches, TSC arise from the interfacial electrochemical reactions owing to the behaviour of metal–polymer–metal systems as primary batteries: this is why one also observes the open-circuit potentials at such interfaces that are characteristic of the electrochemical reactions taking place.

The purpose of this communication is to encapsulate the relevant work that demonstrates that the thermally stimulated currents in such systems arise from electrochemical processes which are central to the valid interpretation of results. Although the paper under discussion (Khare *et al* 2000) mentions this point in passing by giving reference to our work, it does not develop it in sufficient details necessary for the elucidation of the origin of the currents and voltages in these sandwich configurations.

2. Origin of open-circuit voltages and currents in metal–polymer–metal systems subjected to heating

A great deal of experimental work has been done by physicists to delineate the parameters and characteristics of metal (1)–polymer–metal (2) systems subjected to heating; here, the polymer is of an insulating nature such as polyethylene terephthalate (PET), polyvinyl alcohol (PVA), Nylon 66, polyvinyl formal (PVF), polyethylene (PE) and Teflon. On heating such M_1–polymer–M_2 systems above room temperature, so-called spontaneous currents are generated with the accompanying creation of open circuit voltages between the two dissimilar electrodes. Traditionally, physicists have interpreted these open circuit voltages as Volta potential difference between the metals, arising from the different Fermi levels (i.e. work functions) of the metals involved (Wintle 1983). We have shown conclusively, however, that these voltages are, in fact, galvanic in origin and arise from the electrochemical reactions at the metal–polymer interfaces; more specifically, the metal–oxide electrode potentials resulting from the oxidation of the metals involved determine the open circuit voltages (Vijh 1978, 1979, 1986).

The analysis of data in terms of the work function differences (i.e. Volta potentials) of the metals would be entirely valid if one were considering, for example, the transfer of an electron across a gold/vacuum (better than 10^{-9} torr) interface. Even in such metal–vacuum–metal sandwiches, the work function picture would fail if one were using, for example, aluminum electrodes which cannot be made entirely oxide-free even under high vacuum, unless special procedures are used (Vijh 1978, 1979).

In the real case of metal (1)–polymer–metal (2) systems we have, in fact, a number of ions especially H_3O^+, OH^- and organic groups such as –R–OH in the polymer. Such a system involves surface layers (viz. oxides) on the metals and would undergo interfacial redox reactions at

the metal–polymer interfaces. On heating, reactive species such as H_3O^+, OH^- and R–OH groups would be further released by the polymer causing still more pronounced interfacial electrochemical reactions. The system would thus approach a primary battery, with the generation of 'spontaneous' current, albeit low. In such a situation, to invoke work functions of pure, film-free (as under vacuum) metals to explain the phenomenon is quite inconsistent with the obtained experimental conditions. Also, from a point-of-view of purely empirical verification, no relation is observed between the open circuit voltages and the corresponding work function differences when an extensive series of metal–polymer–metal systems is examined, with the exception of some fortuitous cases (Crine and Vijh 1984).

3.   Electrochemical approach: primary battery effects

As described previously (Vijh 1978, 1979, 1986; Crine and Vijh 1984), the systems such as those reported by Khare and coworkers (Khare *et al* 2000), or metal–polymer–metal systems of this type in general, behave as electrolytic cells in which the polymer is the 'reservoir' solvent containing a number of solute species. On heating, these solute species become released and more mobile and make the polymer more conducting thus resulting in its behaviour as an electrolyte.

The electrochemical reactions have been described (Vijh 1978, 1979, 1986) and we have shown that the open circuit voltage, V_{oc}, is linearly related to the difference of metal–oxide potential, $E°$, for the M_1–PET–M_2 system of the two electrodes. This latter parameter is related to the free energy of oxide formation per equivalent $\Delta G_e(M)$ by (Crine and Vijh 1984):

$$\Delta G_e(M) = FE°, \tag{1}$$

where F is the Faraday constant. Thus, it gives (Crine and Vijh 1984)

$$V_{oc} \propto E°(M_1) - E°(M_2) \propto \frac{1}{F}(\Delta G_e(M_1) - \Delta G_e(M_2)). \tag{2}$$

Equation (2) is tested in figure 1 for Nylon 66 as a plot of the maximum V_{oc} vs $\Delta G_e(M_1) - \Delta G_e(M_2)$. Although V_{oc} varies linearly with $\Delta(\Delta G_e(M))$, the slope is not exactly $1/F$ but this discrepancy probably arises from the experimental deficiencies of the procedures used and the uncertainties of the data thus obtained. Identical good fits were also obtained for PET and PVA (Crine and Vijh 1984).

It is mentioned by Khare and colleagues (Khare *et al* 2000) that their work opens up an area that might lead to a practically useful dry cell. In fact, the previous experimental work in this area, it appears, was aimed at exploring the potential of these systems as 'galvanic' cells, i.e. as batteries. However, the fundamental electrochemical theory (Vijh 1973) would show that these systems are more like leaky capacitors than batteries, in view of the extremely low current outputs and high 'electrolyte' resistance. In real batteries, the source of power (current × voltage) are the rationally-chosen interfacial reactions which proceed at relatively high rates on appropriate electrodes embedded in low resistance electrolytes. In M_1–polymer–M_2 systems, the interfacial reactions are merely incidental and are not designed or chosen for power production, and, the internal resistance of these polymer 'electrolytes' is intolerably high especially at room temperatures. Hence these sandwiches have no future as battery systems. Such studies may prove valuable, however, in the interpretation of charge injection phenomena in polymer dielectrics.

The aforementioned remarks are not intended to convey that there is no future for any polymer systems at all as far as the fabrication of batteries ('galvanic' cells) is concerned. In fact, the most promising current work (mostly proprietary) on batteries involves polymeric electrolytes. However, these are specially-formulated ionic polymers
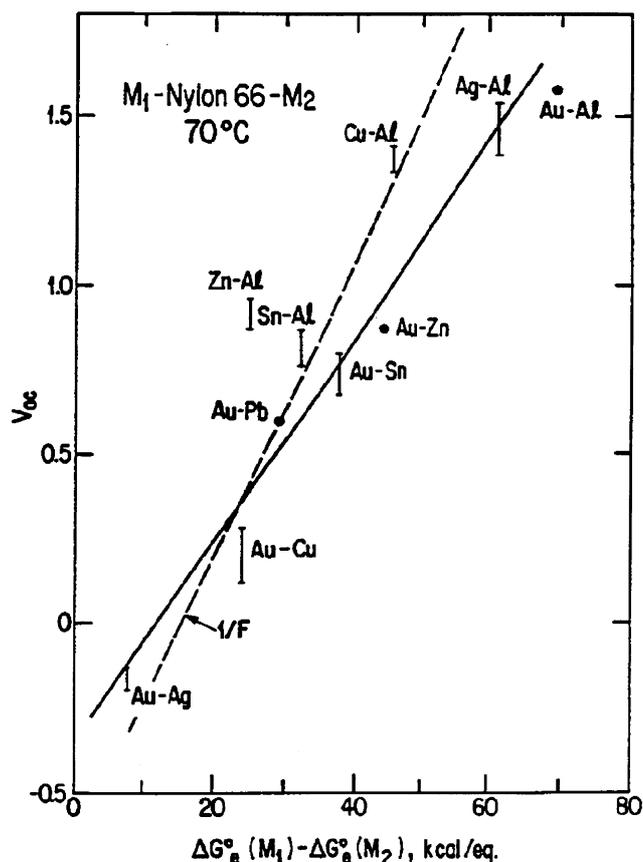

Figure 1.   Maximum open circuit voltage, V_{oc} values observed in several metal 1–nylon 66–metal 2 cells as a function of the difference of free energies of oxide formation. The dashed line corresponds to $1/F$ (Crine and Vijh 1984).

of high conductance and have excellent properties as 'solvating' media for solutes, in contrast to the insulating dielectric polymers used by physicists in M_1–polymer–M_2 systems and investigated by Khare and coworkers in the paper under discussion.

In the context of possible batteries based on polymers, it is crucial to understand the differences between the following three situations.

(I) Metal-insulating polymer–metal sandwiches investigated by Khare *et al* in the paper under discussion and studied by other workers previously (Ieda *et al* 1975; Vijh 1978, 1979), are batteries only nominally because of very high internal resistance and extremely low power outputs (i.e. voltage × current) and unacceptably low power densities. Conceptually, they are better described as leaky capacitors even though the energy storage is not truly 'capacitative' but arises from the interfacial electrochemical reactions i.e. oxidation and corrosion of electrodes etc.

(II) Electronically conducting polymers such as poly-acetylenes which can be used as electrodes in batteries.

(III) Ionically conducting polymers such as polyethylene oxide (PEO) with salts dissolved in it to produce the electrolytes in metal–polymer batteries is under development in many laboratories.

4. Conclusions

An analysis is presented of the work of Khare and coworkers (Khare *et al* 2000) by emphasizing the role of possible battery effects in the thermally-stimulated currents observed by them. The relevance of different metal–polymer–metal systems as possible potential commercial batteries is indicated.

References

Crine J-P and Vijh A K 1984 *Mater. Chem. Phys.* **10** 85

Ieda M, Sawa G, Nakamura S and Nishino Y 1975 *J. Appl. Phys.* **46** 2796

Khare P K, Jain P L and Pandey R K 2000 *Bull. Mater. Sci.* **23** 419

Pillai P K C, Goel T C and Xavier S F 1979 *Eur. Polym. J.* **15** 1149

Vijh A K 1973 *Electrochemistry of metals and semiconductors* (NY: Marcel Dekker)

Vijh A K 1978 *J. Appl. Phys.* **49** 3621

Vijh A K 1979 *J. Appl. Phys.* **50** 3764

Vijh A K 1986 in *Modern aspects of electrochemistry* (eds) J O'M Bockris, B E Conway and R E White (NY: Plenum Press) Vol. 17, Ch. 1

Wintle H J 1983 in *Engineering dielectrics* (eds) R Bartnikas and R M Eichhorn (Philadelphia: ASTM Publications) Vol. IIA