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Note

SPONTANEOUS CURRENT FROM HYGROSCOPIC MATERIALS. A SIMPLE METHOD OF FINDING DEAQUATION TEMPERATURES

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Some polymers, when sandwiched between two metal electrodes, have been reported [1—3] to generate electric currents on heating. In the case of cellulose [3,4], a current has been observed even without heating. The absorbed water in cellulose, in contact with two different metal electrodes, forms a voltaic cell, and thus generates a current. The magnitude of the current becomes greater as the difference in work functions between the two electrodes increases. With heating, sorbed water gets desorbed. These desorbed water molecules, or a particular fraction of them, dissociate into H^+ and OH^- ions, under the influence of the voltaic potential difference between the two electrodes. The rise in current with heating [3,4] is due to one or both of the following reasons:

(i) The liberated ions react with the metals electrochemically.

(ii) Due to the presence of ions, the resistance of the cell becomes lower, with the e.m.f. remaining constant.

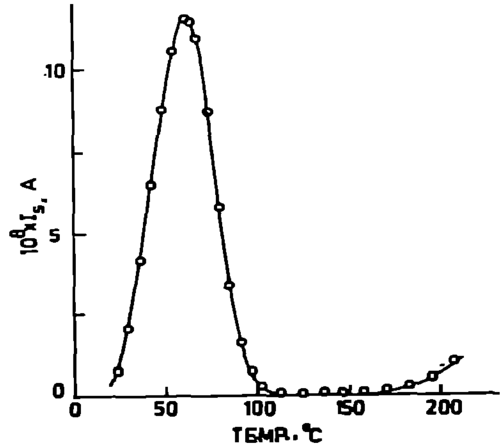

Fig. 1. A typical plot of spontaneous current vs. temperature from the Cu—Cellulose—Al system. Heating rate = 6°C min^{-1}.

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The plots of current vs. temperature for cellulosic materials [3,4] show one peak in the range 50—130° C. This peak is attributed to the water which is desorbed during thermal degradation [5] from room temperature to 150° C. A typical plot for cellulosic polymers is shown in Fig. 1. The second rise in current, above 150° C (refs. 3 and 4, and Fig. 1) is attributed to water dehydrated [5] from equatorial hydroxyl groups in cellulosic units. Assuming that other water-containing materials should also generate similar currents, we have studied poly(vinyl alcohol) (PVA) and $NiSO_4 \cdot x\ H_2O$.

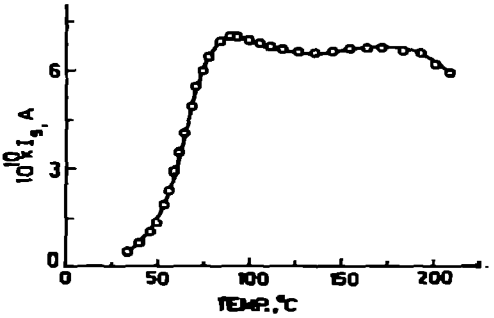
EXPERIMENTAL

PVA samples were solvent (water)-cast films of 40 μm thickness, the area of the electrodes being 4.6 cm^2. Nickel sulphate samples were finely ground compressed powders (pellets, thickness, 1.73 mm, diameter 1.275 cm). The area of the electrodes was the same as that of the pellet. Copper and aluminium were chosen as electrodes. The aluminium electrode was directly connected to earth, and the copper electrode to the electrometer (610 C, Keithley). Under these conditions, the current was positive. The samples were sandwiched between the electrodes, and the assembly was kept in an air oven which could be heated at a constant heating rate by an electric heater and a program controller.

RESULTS AND DISCUSSION

Figure 2 shows the spontaneous current with heating from the PVA. The first peak, at around 92° C, is due to the release of the loosely bound water present in the sample. It has been reported [6] that the water, which is strongly bound in PVA, splits off at a maximum rate at 160° C. The peak observed in the present investigation at around 170° C is attributed to the release of this strongly bound water.

Nandi et al. [7] observed that both the d.c. electrical conductivity and the dielectric constant of $NiSO_4 \cdot 6\ H_2O$ single crystals show large changes near the temperatures 100, 142, 185 and 360° C, and they explained this on the basis of the release of different water molecules deaquated at the respective deaquation temperatures. From TG measurements, they found the deaquation steps as 1 mole, 2 moles, 2 moles and 1 mole at 100, 142, 185 and 360° C, respectively. Let us call these steps A, B, C and D respectively. Our measurements of spontaneous current generation from the nickel sulphate sample, on heating, shows three peaks (Fig. 3). The position of the first peak shifts (in the range 120—132° C) from sample to sample. This peak is assumed to be due to the resultant effect of (i) release of loosely bound water present in the sample, which varies with humidity conditions; and (ii) release of water during step A. The positions of the second and third peaks coincide with the deaquation temperatures of steps B and C, respectively. Step D could not be confirmed as experiments in the high-temperature range could not be carried out.



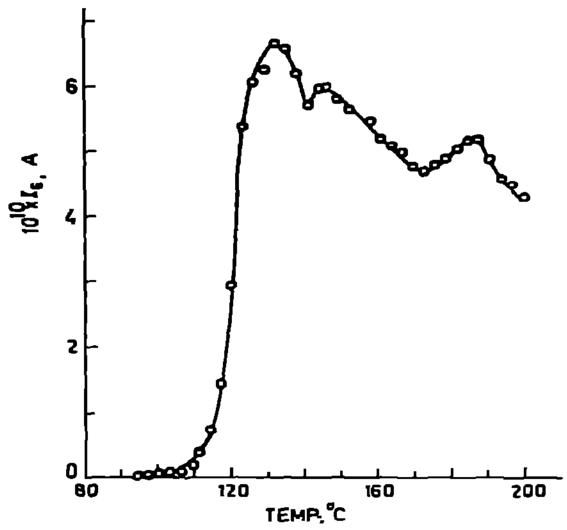


Fig. 2. Plots of spontaneous current vs. temperature for the Cu—poly(vinyl alcohol)—Al system. Heating rate = 3°C min^{-1}.

Fig. 3. Plots of spontaneous current vs. temperature for the Cu—$NiSO_4 \cdot x\ H_2O$—Al system. Heating rate = 3°C min^{-1}.

CONCLUSIONS

The experimental observations in the present investigation lead to the following conclusions:

(i) Hygroscopic materials, organic or inorganic, sandwiched between two metal electrodes form a voltaic cell and generate currents.

(ii) The increase in current with heating is due to the thermo-stimulated release of water molecules bound in the sample.

(iii) The current is in phase with the release of water, that is to say, if at any temperature water is released at the maximum rate, a peak will appear at that temperature in the plot of current vs. temperature.

(iv) The deaquation temperatures can be found by simply measuring the spontaneous current generated on heating.

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