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Potential-Time Profiles in the Initially Homogeneous Unstirred Belousov-Zhabotinskii Reaction with 2,3-Pentanedione

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Heterogeneities for concentration in the titled reaction have been studied using both platinum macro- and microelectrodes, and bromide ion selective macroelectrode.

The most extensively investigated oscillatory chemical reactions are the Belousov-Zhabotinskii(BZ) type reactions.[1] Oscillations are easily measured by the changes in the concentration of bromide ion and the redox potential. The temporal oscillations in a homogeneous, stirred solution have been well understood.[2,3] In this paper the BZ reaction in an unstirred batch reactor was studied using both Pt macro- and microelectrodes to detect the local heterogeneities.

The cerium ion catalyzed BZ reaction with 2,3-pentanedione as a substrate was studied at 30.0(±0.1) °C in an open batch reactor (see Fig. 1). The redox potentials were monitored simultaneously in two sampling volumes of greatly different size using Hg/Hg_2SO_4 electrode as a reference. The local dynamics was monitored by a microelectrode made from a pin point platinum wire as shown in Fig. 1. Monitoring of $[Br^-]$ was carried out with bromide ion selective macroelectrode(ISE). The solution was stirred initially for certain minutes or continuously by a teflon coated magnetic stirbar.

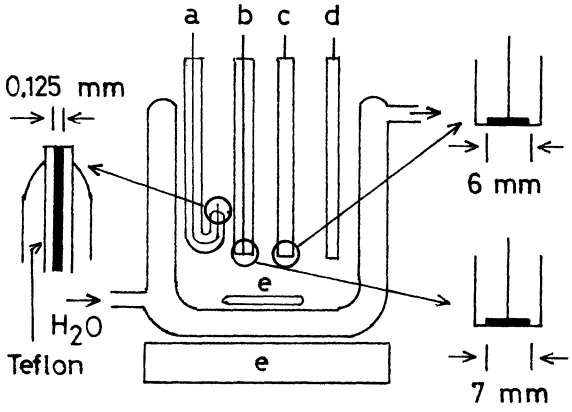

Fig. 1. The experimental arrangement. a:Pt microelectrode, b:ISE, c:Pt macroelectrode, d:reference electrode, and e: magnetic stirrer. Enlarged views of the electrodes are given in the both sides.

A typical record of the potential-time profiles in this BZ system is shown in Fig. 2. After the stirring was stopped, the potentials of ISE and Pt microelectrode began to oscillate irregularly, but that of Pt macroelectrode did not. For comparison, potential profiles for the corresponding stirred system are illustrated in Fig. 3.

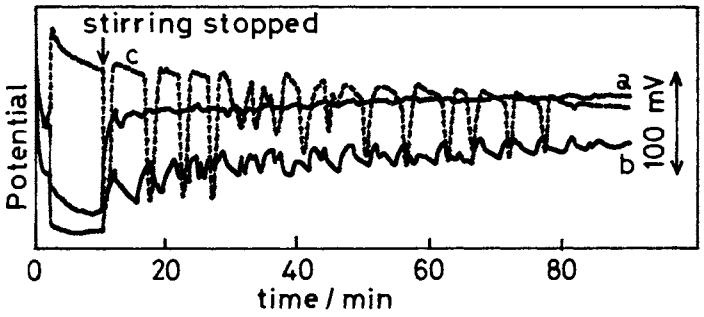

Fig. 2. A typical oscillatory behavior of the unstirred BZ system. Initial concentration: $[H_2SO_4]$ = 0.74 M, $[KBrO_3]$ = 0.14 M, $[Ce(SO_4)_2]$ = 0.0014 M, and [2,3-pentanedione] = 0.032 M. a:Pt macroelectrode, b:Pt microelectrode, and c:ISE. M = mol dm^{-3}

The results of Fig. 2 indicate that the fluctuations (oscillations) are observed only in Pt microelectrode and ISE, but not in Pt macroelectrode. It is probable from the above results that the size of the locally homogeneous region for cerium ion concentration is much smaller than that for bromide ion concentration. Namely, it is considered that the Pt microelectrode indicates the potential in a locally homogeneous region, but the response of the Pt macroelectrode reflects the spatially averaged potential.

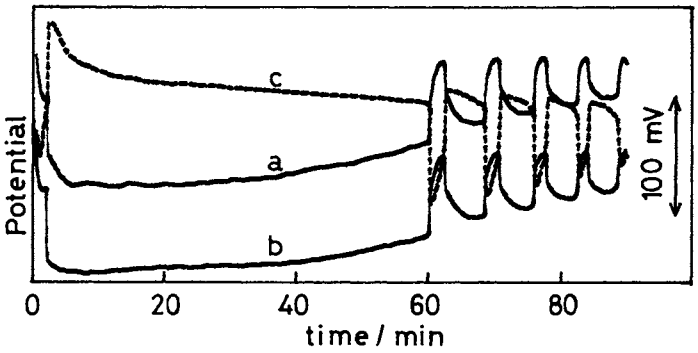

Fig. 3. The same system as that in Fig. 2 except for continuous stirring. a:Pt macroelectrode, b:Pt microelectrode, and c:ISE.

Further studies on the detail and the mechanism are in progress.

References

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