Analysis of the electrolyte diode.
Electro-diffusion and chemical reaction within a hydrogel reactor

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A reaction–diffusion system describing the electrolyte diode is investigated. This consists of a chemically crosslinked polyvinylalcohol (PVA) hydrogel cylinder in which a pH gradient is provided by having an acid and a base maintained at constant concentrations in reservoirs at each end of the one-dimensional reactor. A potential difference of a given strength is also applied across the gel cylinder. Previous experimental studies of the current–voltage characteristics (CVC) have shown two distinct cases, depending on whether a positive or negative potential difference was applied. The slopes of the linear current–voltage response curve are substantially different in the two cases, that in the ‘forward’ case being typically several orders of magnitude greater than that in the ‘backward’ case. Thus the system behaves like a semiconductor diode. The stationary concentration distribution for the different ions is described by a system of reaction–diffusion equations involving migration caused by the electric field. An approximate solution of these equations, using a simplified model, is presented and compared with results obtained by solving the full system numerically. The concentration profiles obtained from the numerical solution confirm the validity of the simplified model.

KEY WORDS: electrolyte diode, reaction–diffusion, electro-diffusion, Nernst–Planck equations

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1. Introduction

Hydrogel reactors are used extensively to study the complex spatial and spatio-temporal structures that can arise in chemical systems. These reactors, so called CFURs (continuously fed unstirred reactors), developed initially in Texas \([1,3]\) and Bordeaux \([2]\), were constructed originally to study reaction–diffusion systems, especially chemical waves and Turing structures in a medium free of convection. They have subsequently proved to be an extremely versatile experimental procedure and have been used to show\[43\]
that chemical systems, appropriately arranged, can sustain a wide variety of patterning processes. Much of this work is reviewed in [4,5].

A new version of this reactor, in which gradients of electrical potential as well as concentration gradients can be maintained, has been devised recently by Noszticzius and co-workers [6–8]. The main part of this reactor consists of a chemically crosslinked polyvinylalcohol (PVA) hydrogel cylinder in which a pH gradient is provided by having an acid and a base maintained at constant concentrations in reservoirs at each end of the one-dimensional reactor, HCl and KOH being used in the experiments. A potential difference of a given strength is also applied across the gel cylinder. The acid and base dissociate into their respective ionic components, specifically $H^+$, $OH^-$, $Cl^-$ and $K^+$. These components diffuse and migrate under the action of the applied electric field, producing an electric current within the reactor. The experimental results are presented in terms of the dependence of this current on the applied potential difference.

The experiments [6] were performed specifically with HCl and KOH having equal concentrations $c_0$ in their respective reservoirs at the ends of the reactor (with a zero concentration of the other reactant also being maintained there). Two distinct cases were seen, depending on whether a positive or negative potential difference was applied. In the ‘forward’ case the electric field was applied so that it is the $K^+$ and $Cl^-$ ions from the KOH and HCl solutions that migrate through the reactor, where they form a KCl solution, at concentration $c_0$. In the ‘backward’ case the tendency is for the $OH^-$ and $H^+$ ions (from the KOH and HCl solutions respectively) to migrate into the reactor. In both cases, a linear current–voltage response curve is seen for sufficiently large applied voltages. However, the slopes of these curves are substantially different in the two cases, that in the ‘forward’ case being typically several orders of magnitude greater than that in the ‘backward’ case. Thus the system behaves like a semiconductor diode.

One reason suggested for this marked difference between the two cases is that, in the ‘forward’ case, the current is carried mostly by the $K^+$ and $Cl^-$ ions (with the contribution from the $H^+$ and $OH^-$ ions being negligible). These ions achieve the constant concentration $c_0$ throughout most of the reactor gel, which consequently has a relatively low impedance. In the ‘backward’ case, the applied electric potential is such that the $K^+$ and $Cl^-$ ions cannot migrate far from their respective ends. The $H^+$ and $OH^-$ ions are now the ones that are “pulled” into the reactor under the effect of the electric field, where they react to form a zone of pure water. This zone, where there are only low concentrations of $H^+$ and $OH^-$ ions because of the reaction between them, has a relatively high impedance and it is where the majority of the potential drop occurs. Thus relatively large voltages need to be applied to produce a significant current.

A theoretical explanation for these phenomena was proposed in [6] and [8]. The stationary concentration distribution for the different ions is described by a system of reaction–diffusion equations involving migration caused by the electric field. An approximate solution of these equations, using a simplified model, was presented in [6,8]. The basic assumption behind this model is that the reaction between the $H^+$ and $OH^-$ ions takes place in very narrow reaction layer(s), negligible in extent compared to the total length of the reactor. Therefore, in the simplified description the one-dimensional...