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Potassium cation induced ionic diode blocking for a polymer of intrinsic microporosity | nafion “heterojunction” on a microhole substrate

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ABSTRACT

“Heterojunction” ionic diodes based on a Nafion cation conductor and a polymer of intrinsic microporosity (PIM) interfaced at a 6 μm thickness polyethylene-terephthalate (PET) film with 20 μm diameter microhole exhibit rectification effects in cation (K^+) flux. When combined with the precipitation reaction of potassium cations with perchlorate anions to give insoluble $KClO_4$ (solubility product ca. 1.05×10^{-2} M^2 at 25 °C) at the PIM | Nafion interface, inversion of the rectification/diode effect occurs and the formerly “open” state changes into a “closed” state due to blocking of ion flow. The localised interfacial precipitation reaction is due to up to three orders of magnitude accumulation of K^+ at the PIM | Nafion interface and shown to be fast and reversible. The effects of K^+/ClO_4^- concentration and of Na^+ interference are considered. The blocking process within the heterojunction ionic diode is suggested to be dynamic/fast and potentially useful as a diode sensor mechanism based on solubility product dependent precipitation.

1. Introduction

Polymer interfaces provide interesting reaction environments [1,2] related (at least a little bit at functional level) to biological membrane interfaces, where the flux of ions can trigger chemical reactions and *vice versa* (e.g. in ATPases [3]). We have recently investigated polymer interfaces in microhole “heterojunctions” [4] where cation flux driven by applied potential is high in one direction but low in the opposite direction. The resulting rectification or “ionic diode” effect can be substantial and optimisation of this effect has been suggested to lead to new desalination [5] and energy harvesting [6] technology. The applied potential-dependent reaction conditions at these polymer micro-interfaces are of interest in view of chemical reactions that can be triggered and electrochemical mechanisms that may contribute to sensor development. Here a process sensitive to potassium, K^+, is investigated.

The emerging field of ionic diode devices [7,8] has initially been based mainly on gel-electrolyte interfaces [9], which led to ionic rectifier [10] and amplifier [11] processes based on ionic currents. Today, the ionic diode field is dominated by nanochannel [12], nanocone [13,14], and nanopore [15,16] devices that mimic much more closely the biological ion channels located in membranes [17]. A wide range of nano-architectures [18,19] and applications [20] has been proposed, pH-switchable devices have been developed [21], and a perspectives review has appeared with focus on stimuli response “iontronics” [22]. Recently, when investigating microporous polymers, we observed micro-scale ionic diode behaviour also for asymmetrically deposited ionomers on microholes in polyethylene-terephthalate (PET) substrates [23]. Both “cationic diodes” or “anionic diodes” (with cation or anion charge carriers, respectively) were observed with the microporous ionomer based on either Nafion [24], cellulose or modified cellulose [25,26], or on polymers of intrinsic microporosity (PIMs) containing amines, which when protonated provide intrinsic positive charges [27].

Polymers of intrinsic microporosity (PIMs) offer a novel class of highly porous materials with excellent processibility [28,29]. The molecular structure of these materials is based on a highly rigid and

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contorted polymer/molecular chain that prevents packing and ensures microporosity [30]. Important examples have been PIM-1 [31] and Tröger Base PIMs [32]. Materials such as PIM-EA-TB (EA = ethanoanthracene and TB = Tröger base, see molecular structure in Fig. 1) have been developed with tertiary amine functionality in the backbone [33]. Most applications proposed for PIMs have been in gas separation [34,35] and storage [36], but interesting new applications now also emerged in organocatalysis [37], electrochemistry [38–40], reagentless electro-chemiluminescence [41], and in energy storage [42].

We have recently demonstrated that a Nafion film deposited asymmetrically onto a microhole (in PET) is sufficient to trigger

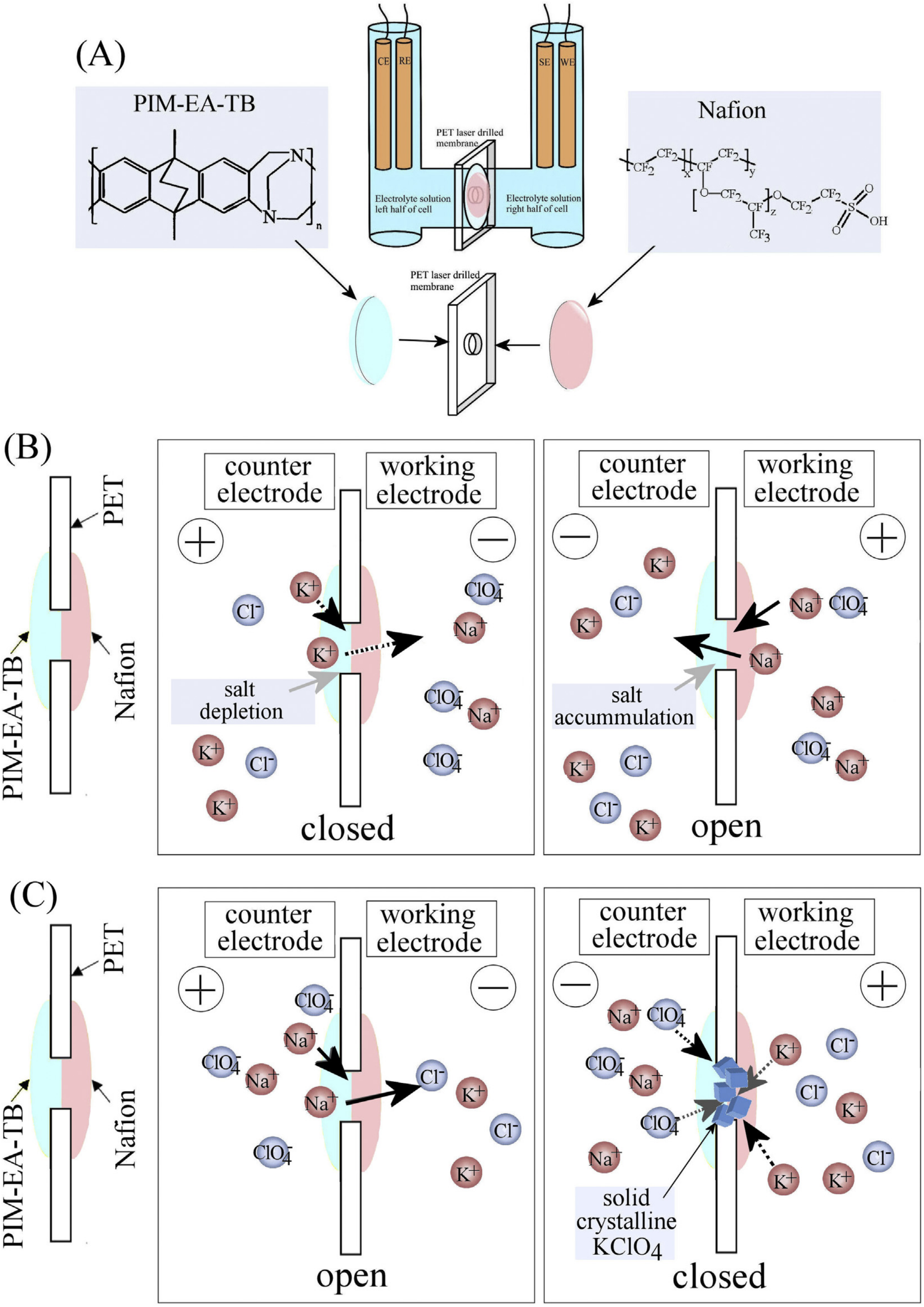

Fig. 1. (A) Schematic drawing of the two-compartment four-electrode electrochemical cell with a microhole interface separator. For heterojunction experiments Nafion is applied on the working electrode side and PIM is applied on the counter electrode side. (B) Operational scheme for the “normal” cationic diode effect. (C) Operational scheme for the “inverted” cationic diode effect with $KClO_4$ precipitation and blocking.