Electrochemical Detection of Single Phospholipid Vesicle Collisions at a Pt Ultramicroelectrode

The collision behavior of single unilamellar vesicles, composed of a bilayer lipid membrane (BLM), on a platinum (Pt) ultramicroelectrode (UME) by two electrochemical detection methods is reported. In the first method, the blocking of a solution redox reaction, induced by the single vesicle adsorption on the Pt UME, can be observed in the amperometric i-t response as current steps during the electrochemical oxidation of ferrocyanide. In the second technique, the ferrocyanide redox probe is directly encapsulated inside vesicles and can be oxidized during the vesicle collision on the UME if the potential is poised positive enough for ferrocyanide oxidation to occur. In the amperometric i-t response for the latter experiment, a current spike is observed. Here, we report the vesicle blocking (VB) method as a relevant technique for determining the vesicle solution concentration from the collisional frequency and also for observing the vesicle adhesion on the Pt surface. In addition, vesicle reactor (VR) experiments show clear evidence that the lipid bilayer membrane does not collapse or break open at the Pt UME during the vesicle collision. Because the bilayer is too thick for electron tunneling to occur readily, an appropriate concentration of a surfactant, such as Triton X-100 (TX100), was added in the VR solution to induce loosening of the bilayer (transfection conditions), allowing the electrode to oxidize the contents of the vesicle. With this technique, the TX100 effect on the vesicle lipid bilayer permeability can be evaluated through the current spike charge and frequency corresponding to redox vesicle collisions.

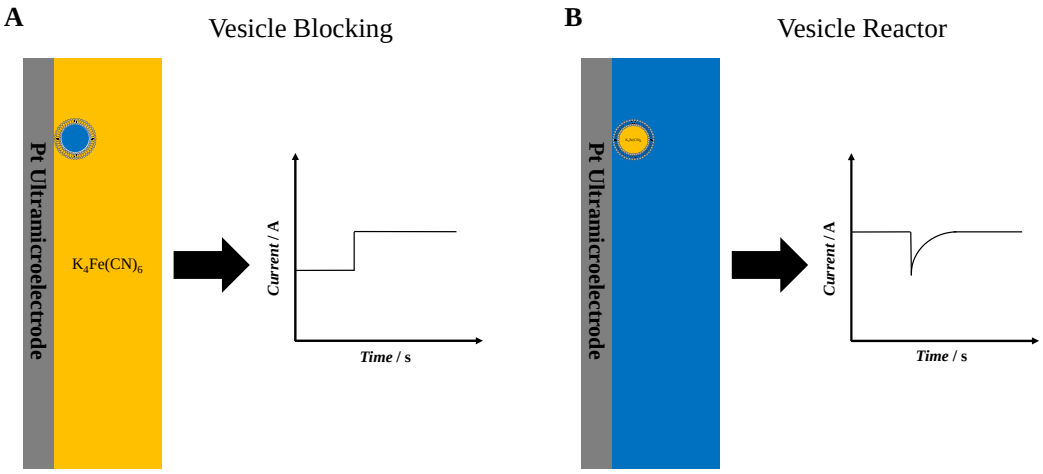

Figure 1. Schematic representation of the two reported vesicle collision techniques at a Pt UME where the potential applied is at +0.6 V vs. Ag/AgCl, and the oxidation currents are plotted in the negative direction (A) Electrochemical oxidation of $Fe(CN)_6^{4-}$ in aqueous solution (negative current) is partially blocked by single vesicle blocking (VB) which produces an anodic current step . (B) Electrochemical oxidation of $Fe(CN)_6^{4-}$ encapsulated inside the vesicle reactor (VR) gives an anodic current spike.