

Supporting Information, Control of Selective Ion Transfer across Liquid-Liquid Interfaces: a Rectifying Heterojunction Based on Immiscible Electrolytes

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S1. Control Experiments

In order to elucidate the role of the electrolytes in isolation, and in their interaction with the electrode and the liquid/liquid interface several control experiments were performed. For the electrical measurements, two Ag/AgCl electrodes were inserted in both oil and water phases. They were connected to a Keithley 2601 source meter inside a Faraday cage. The electrostatic potential at the nitrobenzene phase electrode was varied from -0.5 to +0.5 Volts in 50 small steps at a regular time intervals and the associated electric current was recorded at each one of these steps. The scanning speed is defined as how rapidly voltage steps were varied at each point, and the responsive current through the interface was recorded with respect to the reference electrode placed at the aqueous phase. Figs. S1(a), S1(c), and S1(d) show the I-V curves of the water/nitrobenzene biphasic system in the absence of any added salt, with only TEABr, and with only TBAClO₄, respectively. The electrical currents measured in all these three control experiments are 1-2 orders of magnitude smaller than the current measured when both salts are present. In addition, all I-V curves are monotonic linear, and do not show significant rectifying effect. It is also worth mentioning that TEABr alone would precipitate from the water side of the interface (Fig. S1(b)), which completely dissolves after adding TBAClO₄. The biphasic system with both salts added appears clear.

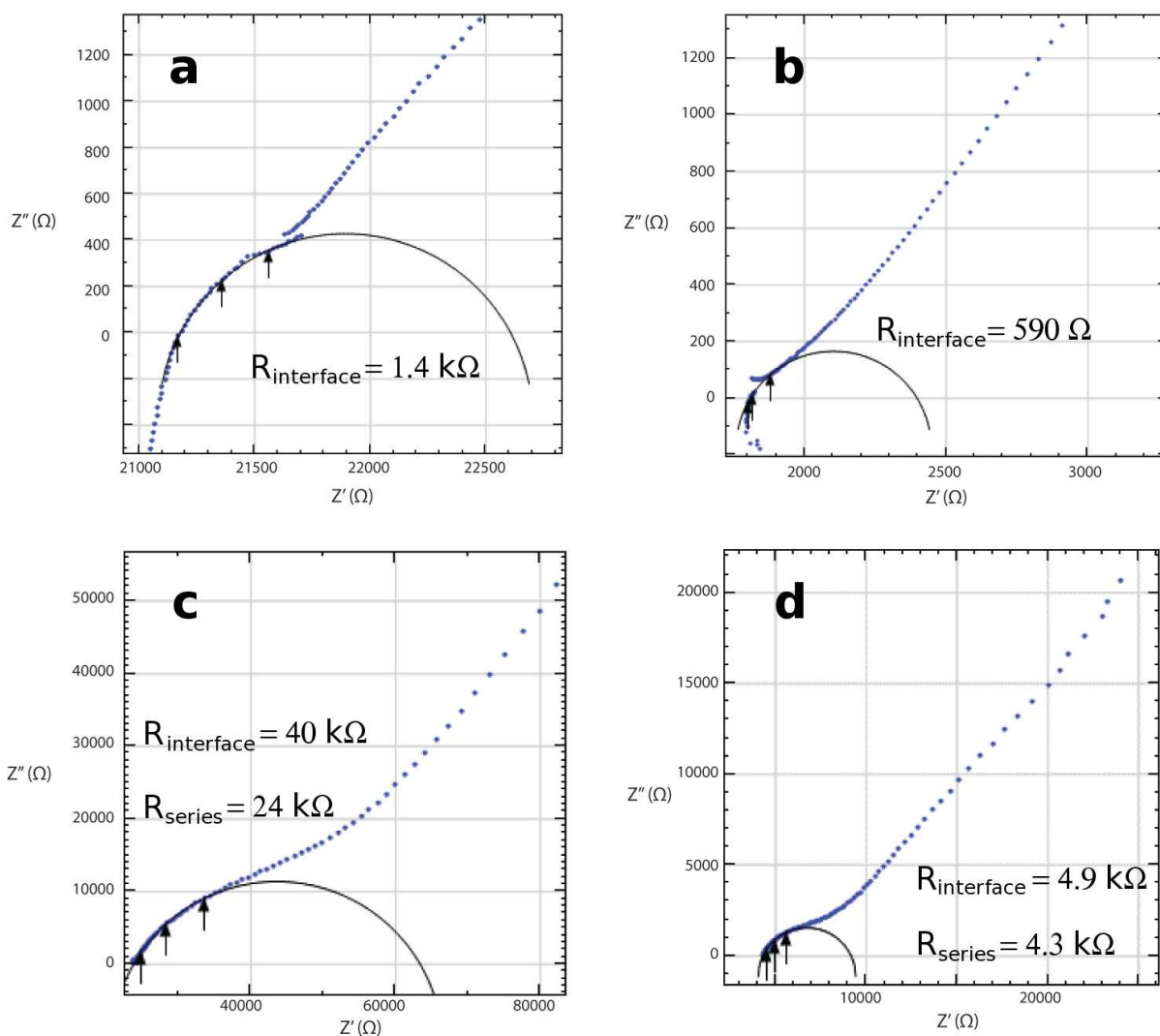


Figure S0. (Color online) The wire-solution interfacial resistances are estimated from the diameters of the electrochemical circles measured in the individual solutions of (a) 10 mM TBAC in nitrobenzene, and (b) 10 mM aqueous TEAB. (c) The impedance spectrum for the oil-water junction at 10 mM salt concentrations displays a considerably higher interfacial resistance than the spectra of the constituents. The difference, which represents the overwhelming majority of interfacial resistance in the system, is attributed to the oil-water interface. However, the ability of the device to carry current is limited by a large series resistance. The diagonal tail shape of the curve at low frequency indicates that the device performance is limited by the diffusion of ions through the bulk liquids. (d) When the electrolyte concentration is 100 mM, a more pronounced semicircle and lower series resistance are observed, indicating that the limitations are improved upon. Interfacial resistance is also lowered.

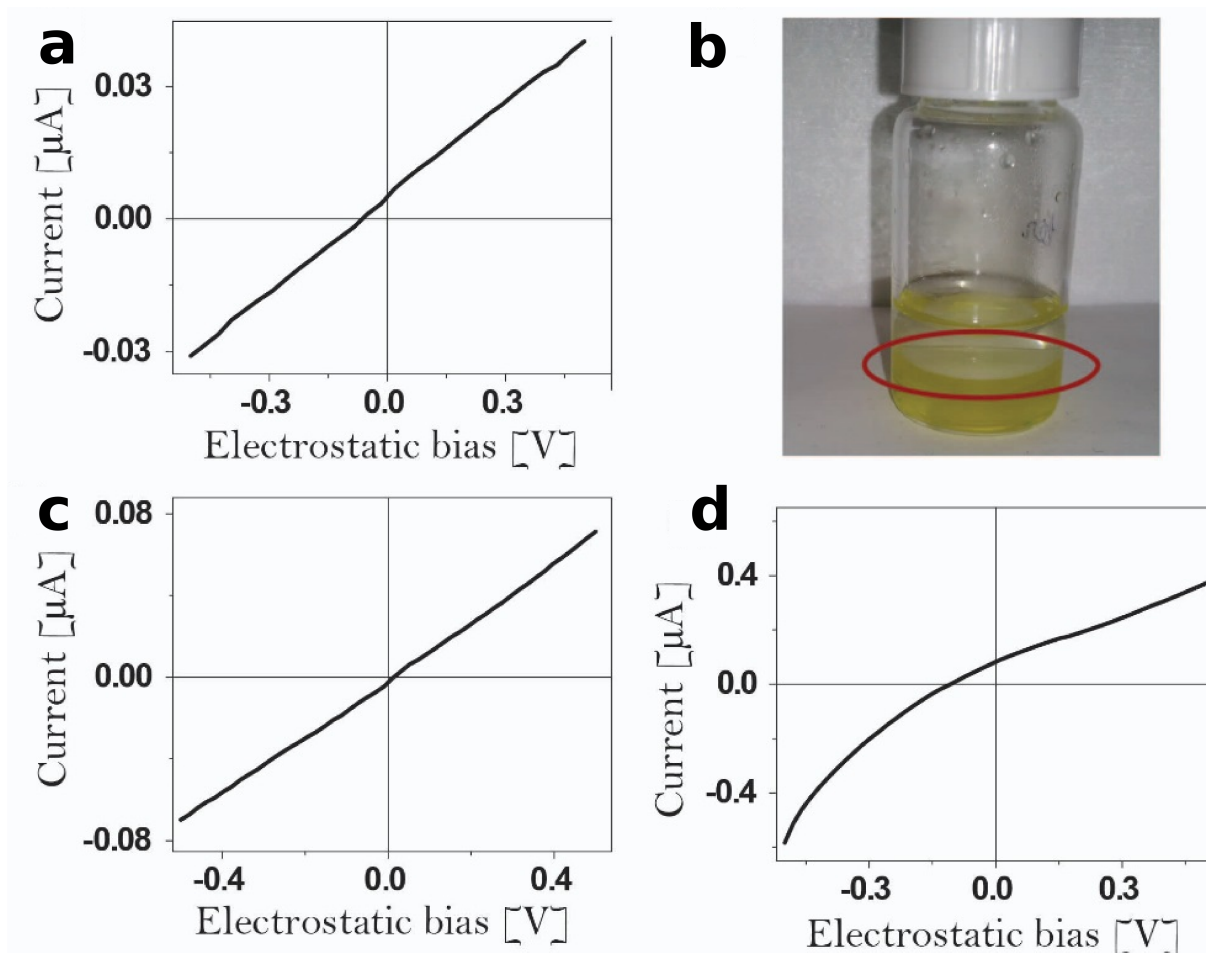


Figure S1. (Color online) Electric currents at the electrified water/nitrobenzene liquid interface as a function of the applied voltage bias recorded in the control experiments. (a) I-V curve in the absence of any added salt. (b) Photograph of the TEABr salt precipitated at the water/nitrobenzene interface when only this electrolyte is present in the system. (c) I-V curve in the presence of TEABr alone. (d) I-V curve in the presence of TBAClO₄ alone. The scanning speed was 0.02 Volt/sec.