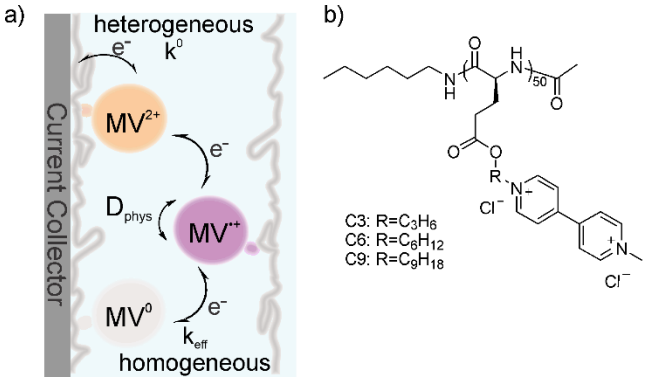
Electron Transport in Redox-active Polypeptides

Alexandra D. Easley, Tan P. Nguyen, Cheng-Han Li, Shih-Guo Li, Miao Qi, Nari Kang, Sarosh Khan, Soon-Mi Lim, Yohannes H. Rezenom, Shaoyang Wang, David K. Tran, Jingwei Fan, Rachel A. Letteri, Xun He, Lu Su, Cheng-Han Yu, Karen L. Wooley, Daniel Tabor, and Jodie L. Lutkenhaus

Within a few decades, lithium-ion batteries have revolutionized technologies facilitating the development of new portable devices and electric vehicles. However, this rapid technology growth has exceeded the mining ability of lithium, cobalt and other mineral ore resources. To reduce this reliance on strategic elements, organic-based electroactive materials such as poly(TEMPO methacrylate), which has a nitroxide radical that can reversibly store energy through a reduction/oxidation mechanism, have received considerable attention. In this talk, a metal-free all-polypeptide-based battery is demonstrated, in which viologens and nitroxide radicals are incorporated as redox-active groups along polypeptide backbones to function as anode and cathode materials, respectively. The resulting battery had an initial capacity of 37.8 $mA \cdot h \cdot g^{-1}$ (85% of the theoretical capacity) and a maximum cell voltage of 1.6 V. The redox-active polypeptides were stable during battery operation and could be subsequently degraded on-demand in acidic conditions. With proof of operational stability and on-demand degradation, the structure-electron transfer relationship for the viologen-based polypeptides is investigated. Three viologen-based polypeptides with varying linker spacing are studied using both experimental and computational methods. Experimentally, the heterogeneous and homogeneous electron transfer rates are evaluated with electrochemical methods including cyclic voltammetry and chronoamperometry. Computationally, the diffusion of the viologen group is determined from trajectory analysis for the three polypeptides and related to their experimentally observed charge-transport behavior. Finally, the electron transfer kinetics impact on battery performance is elucidated with half-cell batteries and varying rates of charge-discharge.



a) The diffusion cooperative electron transfer for the viologen pendant groups in a thin film. b) The three viologen-based polypeptides with varying linker spacing.