

Operando Raman Spectroscopy for Electrochemical Flowing Systems

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Generation of electricity from renewable sources is crucial for achieving the transition to a sustainable and decarbonization energy system. While solar and wind power are becoming increasingly popular, their intermittency requires the deployment of efficient and cost-effective energy storage systems (ESSs) to match energy production and demand. Among the various EESs, redox flow batteries (RFBs) that are featured by their independent scalability of energy and power are promising ESSs candidates for stationary energy storage application. The all-vanadium redox flow battery (AVRFB) is currently the state-of-art of RFB, but the large-scale implementation of AVRFBs presents an intrinsic challenge; vanadium is considered a critical material. Aqueous organic redox flow batteries (AORFBs) gaining much interest as vanadium-based species are replaced by organic redox-active species. While many organic molecules have demonstrated suitable redox potentials, kinetics and solubilities, their cycle stability should be further improved for large-scale deployment.¹ Therefore, advanced techniques are required to investigate the capacity fading mechanisms in operando conditions.

In this contribution, the implementation of Raman spectroscopy for AORFBs will be discussed. Raman spectroscopy is a very useful technique that provides chemical information on redox-active molecules. Surprisingly, this powerful analytical technique has not been exploited in RFBs despite its intrinsic advantages to investigate highly concentrated solutions of strongly colored active species over more commonly used UV-Vis spectroscopy. Overall, the aim of this contribution is to promote the use of Raman spectroscopy within the RFB community by disclosing technical details for its implementation and discussing a couple of case-studies (Figure 1). Specifically, this contribution will be structured in three sections. First, the specific design, fabrication and practical implementation of Raman spectroscopy in a redox flow system for RFB research will be disclosed. Second, Raman spectroscopy will be used to monitor the state-of-charge and potential degradation of the catholyte of ferrocyanide-based redox flow batteries (both in alkaline and neutral pH). Finally, results on degradation of viologen-based anolytes in the unavoidable presence of oxygen traces² will be presented. Importantly, the methodology presented here may be of interest to other communities since it is implementable for other electrochemical flowing systems such as semi-solid flow batteries, electrochemical oxidation of pollutants, electrosynthesis, etc.

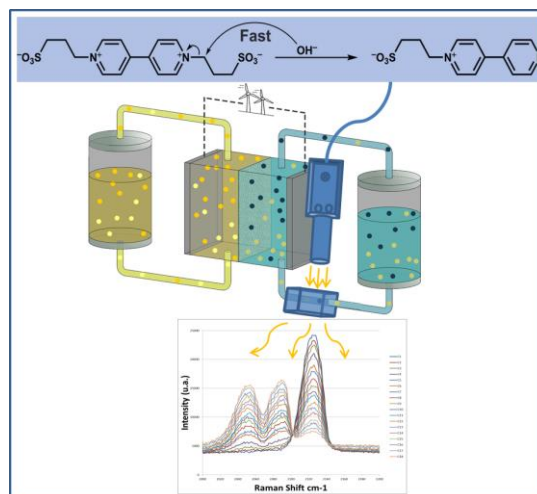


Figure 1. Scheme of RFB coupled with Raman spectroscopy, and degradation mechanism

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