

Stability Enhancement of Viologen Derivatives for Redox Flow Batteries by Molecular Engineering

Rubén Rubio-Presa^{1,2*}, Lara Lubián^{1,2}, Roberto Sanz¹, and Edgar Ventosa^{1,2}

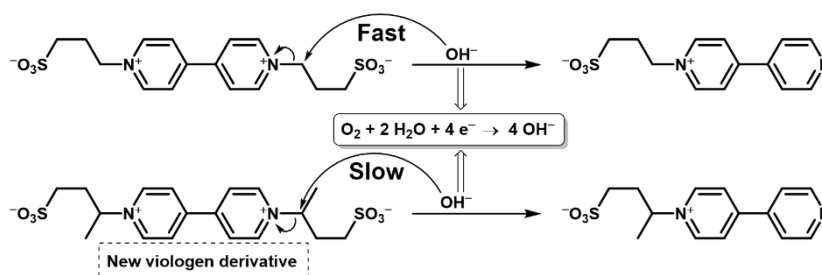
¹ *Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos s/n, E-09001, Burgos, Spain*

² *International Research Center in Critical Raw Materials-ICCRAM, Universidad de Burgos, Pza. Misael Bañuelos s/n, E-09001, Burgos, Spain*

*email: rrpresa@ubu.es

Redox flow batteries (RFBs) have emerged as highly promising energy systems designed for long-term stationary energy storage, distinguished by their remarkable capability for independent scalability of both energy and power. Among RFBs, all-vanadium flow batteries currently occupy the forefront of this technology. However, the use of vanadium, considered a critical material by the EU and the US, represents a significant drawback, leading to growing interest in exploring alternatives. One of the most promising approach is the substitution of vanadium species by highly soluble organic redox species. Within this context, viologen derivatives stand out as the most prominent anolytes, specifically for neutral media, due to their advantageous combination of suitable redox potential and solubility. However, practical implementation reveals a notable disadvantage: viologen derivatives undergo accelerated decomposition in the presence of oxygen, even with the inevitable trace amounts of oxygen present in large-scale RFB systems.

As a first step to address this drawback, we carried out an exhaustive examination of this primary degradation mechanism of viologen derivatives, subsequently proposing an efficient, accessible and rapid method to evaluate their stability in relation to this decomposition process. Since the cleavage of the *N*-substituent turned out to be the main route for the degradation of viologen, we proposed the synthesis of a new viologen derivative that presents an alkylsulfonate chain attached to each *N* atom of the bipyridinium moiety through a secondary carbon atom instead of a primary one. Through this increase of steric hindrance around *N* atoms, we successfully mitigate chemical degradation in the presence of oxygen, resulting in a notable 3-folds reduction in capacity fading. This result serves as a compelling demonstration of how molecular engineering can effectively enhance stability.¹



References

[1] R. Rubio-Presa, L. Lubián, M. Borlaf, E. Ventosa, R. Sanz, Addressing practical use of viologen-derivatives in redox flow batteries through molecular engineering, *ACS Materials Lett.*, 5 (2023) 798.

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