

Electrochemically induced protein-based process for rare earth extraction and separation

Utkarsh Kapoor (team leader),¹ Karen E. Wawrousek,¹ and Caleb M. Hill²

¹Department of Chemical and Biomedical Engineering, University of Wyoming, Laramie, USA

²Department of Chemistry, University of Wyoming, Laramie, USA

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1. Description of research problem

Rare earth elements (REEs) comprising the lanthanide chemical group play an irreplaceable role in modern technologies. The U.S. Department of Interior has designated sixteen of the seventeen REEs as critical materials¹ and the U.S. Department of Energy has highlighted five REEs in particular (Tb, Dy, Eu, Nd, and Y) as vulnerable for supply and critical for clean energy technologies.² While REEs are relatively abundant in the Earth's crust, the extraction and subsequent separation of individual REEs represent a challenging yet essential task for the growth and sustainability of renewable energy technologies.

Currently, REE separation is dominated by a two-phase metallurgical process, which is organic solvent-intensive and hence requires high capital expenditure, longer equilibration time, and incurs higher energy costs, losses of extractant that poses severe environmental burdens.³ It is thus imperative to develop new process methodologies that enable environmentally friendly REE extraction.

Previously, it has been shown that a small (~12 kDa) protein, *lanmodulin* (*LanM*), not only possess remarkable preference toward middle–light REE over heavy REE but also selectivity for REEs against non-REE cations.⁴ More recently, it has been shown that *LanM* forms a homodimer that further facilitates lanthanide binding,⁵ however, information regarding its implementation in a REE separation process is not known. We believe such a biobased system with a preference for REEs can be further exploited for efficient separation of light/heavy REE groups or even important REE pairs. Furthermore, we can utilize homodimerization of *LanM*, a principle that is inherent in nature, to our advantage in a separation process. Thus, as an important step toward overcoming the technical and environmental limitations of current REE processing methods, ***we propose to develop a biomaterial based all-aqueous REE extraction and separation scheme (Fig. 1)*** that will leverage electrochemically induced binding/desorption driving force (instead of a chemical driving force that poses an issue of generating secondary liquid waste) to provide better control and further enhance REE selectivity of *LanM* homodimer.

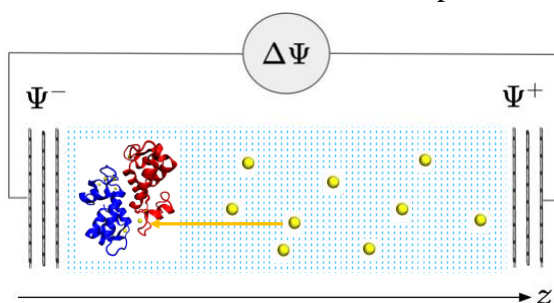


Fig. 1. Proposed scheme with *LanM* homodimer (red and blue) and REE cations (yellow) in an electric field.

2. Short-term objectives and work plan

While the *LanM* protein homodimer is known to bind to lanthanides with incredible binding affinity, ***the overarching goal*** of this proposal is to control and further enhance REE selectivity of *LanM* homodimer using an electrochemical scheme. ***The central hypothesis*** is that external stimulus (like

¹ 2022 Final List of Critical Materials (2022). USGS, Dept. of the Interior

² U.S. Department of Energy. Critical Materials Strategy, 2010.

³ Xie, F.; Zhang, T. A.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* 2014, 56, 10–28

⁴ Cotruvo, J. A.; Featherston, E. R.; Mattocks, J. A.; Ho, J. V.; Laremore, T. N. Lanmodulin: A Highly Selective Lanthanide-Binding Protein from a Lanthanide-Utilizing Bacterium. *J. Am. Chem. Soc.* 2018, 140 (44), 15056–15061.

⁵ J. A. Mattocks, J. J. Jung, C.-Y. Lin, Z. Dong, N. H. Yennawar, E. R. Featherston, C. S. Kang-Yun, T. A. Hamilton, D. M. Park, A. K. Boal, J. A. Cotruvo, Enhanced rare-earth separation with a metal-sensitive lanmodulin dimer. *Nature* 618, 87–93 (2023).

electric field or charged surfaces) can be used to fine-tune mobility of LanM and the sensitivity of binding/desorption of the REE groups. We are particularly interested in creating and evaluating a protein-based prototype electrochemical process for separation of light-middle vs. heavy REEs and selectivity recovery between REE vs. non-REE cations. To this end, this proposal seeks to achieve the following **specific objectives**: 1) To gain a fundamental understanding of protein structure and dynamics in solution (e.g., fine-tuned immobilization onto a support vs. migration of protein towards REE ions) and light-middle vs. heavy REE ions vs. non-REE ions transport in solution, and 2) To characterize REE binding affinities to the LanM homodimer (e.g., interfacial stabilization between solvent, ion, and protein molecules, and solvation and de-solvation of the target REEs), both in response to electrochemical stimuli.

First, Kapoor lab will use computer simulations to answer these quandaries. Employing state-of-the-art molecular dynamics simulations at two spatiotemporal scales: atomistic and coarse-grained, coupled with *ab initio* calculations, we will cover the range of REEs binding to the LanM homodimer and its mutants (e.g., we will design surface mutants to create acidic/basic patches to fine-tune the migration of LanM and its binding to REEs) by examining the structure, local coordination environment, solvation energies, binding affinities and dynamics of how individual REE ions bind to free/immobilized LanM homodimer in presence of electrochemical stimuli, with the aim to identify molecular features that allows for selective binding of particular REEs. It is possible that standard force field computational models do not capture the molecular interactions realistically. If so, we will use experimental results (specifically ion binding data as mentioned below), to make necessary modifications and refine the nonbonded interactions.

Based on the computational results, the Wawrousek lab will generate the best LanM homodimer (wildtype or its surface mutants) and express them in *E. coli* following published protocols. The protein will be purified and, if warranted, immobilization will be achieved on an agarose support. Next, the protein will be incubated with a solution containing REE and non-REE ions, and ion binding to LanM will be quantified by ICP-OES and ICP-MS at the UW Geochemistry Analytical Laboratory to assess LanM REE binding and selectivity with or without the presence of external electrochemical stimulus.

Lastly, the Hill lab will design, construct, and evaluate practical electrochemical cells to carry out REE separations using the best LanM homodimer system. These cells will consist of an REE-containing electrolyte, a chemically inert electrode, and an electrode onto which the LanM is attached via specific and/or non-specific adsorption mechanisms. Through application of an electrochemical bias, REE ions will be driven to bind with the surface-immobilized LanM at one electrode while oxygen is evolved at the other electrode; under reverse bias, the REE ions can then be freed into an eluent stream while evolving hydrogen at the other electrode. The efficacy of this electrochemical process will be evaluated at bench scale via cyclic voltammetry (to determine energetic parameters describing REE binding) and bulk electrolysis experiments (to evaluate Faradaic efficiency and practical viability). The overall goal is to demonstrate proof-of-concept for the prototype system, which will be critical to our follow-up proposals.

3. Long-term benefits and list of potential future partners

The preliminary results will open the door to collaborative proposals among departments within our college and beyond. Once we demonstrate the proof-of-concept, we plan to collaborate with CEGR scientists on campus and USGS scientists that have characterized REE concentrations in aqueous environments to identify and test REE-containing samples from the environment.

4. List of funding sources and programs that could fund the proposed research

The obtained preliminary results will strongly help capture external grants from several agencies, including Department of Energy, National Science Foundation (for e.g., CBET program), American Chemical Society Petroleum Research Fund, and/or NASA. Two proposals to NASA EPSCoR on related work, one with (PI Wawrousek, co-PI Utkarsh) and another with (PI Caleb, co-PI Utkarsh) are pending.

Budget and budget justification

The following table summarizes the budget requested (personnel, supplies and materials, travel, and total) for this project. The requested funds will be used to support an undergraduate student and partially cover the student's stipend during the one-year funding period. PI Kapoor and co-PIs Wawrousek and Hill will all advise the student on this project year round via biweekly/monthly meetings. A total of \$14,000 is requested for supplies and materials for PI and co-PIs. Funds are also budgeted for the student/faculty to travel to the local conference to disseminate the results of this work. Lastly, \$1,000 each, including fringe, for PI and co-PI's summer salary is budgeted.

	1. Request
2. Labor	
Faculty Labor for PI and each Co-PI – Summer Salary	\$2,129
Benefits (40.9%)	\$871
One Undergraduate Student Labor - Stipend	\$5,000
3. Other Costs	
Supplies and Materials for Co-PI in Chemistry	\$6,500
Supplies and Materials for Co-PI in Chemical and Biomedical	\$6,500
Supplies for PI	\$1,000
Travel funds to disseminate results at a local conference	\$3,000
4. Total Cost	\$25,000