

THE EFFECT OF OSMOTIC PHENOMENA ON THE STABILITY OF ENERGY STORAGE SYSTEMS IN THE COMPOSITION OF LIQUID ELECTROLYTES SEPARATED BY A POLYMER MEMBRANE

Matiukha V., Linyucheva O.

National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”

Russia's aggressive war against Ukraine has worsened the global energy situation. In the context of climate change and technological progress in renewable energy sources (RES), most developed countries have urgently begun developing plans to reduce their dependence on fossil fuels. For example, the REPowerEU Plan [1] sets an ambitious goal of achieving climate neutrality by 2050.

Although renewable energy sources (RES) have obvious advantages, they also have certain drawbacks, the main one being the unpredictability of energy generation over time, due to dependence on weather conditions, seasons, and the geographical features of the location where RES facilities are situated. A solution to this problem is the creation of systems for balancing the transmission of generated energy. High-capacity batteries [2] can serve as a buffer between generating facilities and the integrated power grid, accumulating electricity when production exceeds consumption and delivering it when generation falls short of demand. One variant of this technology is redox flow energy storage systems. The principle of operation of these batteries involves the circulation of electrolytes through porous electrodes, where ions of electrolyte A (anolyte) are oxidized during charging, and ions of electrolyte B (catholyte) are reduced during discharging. A polymer membrane must prevent electrolyte mixing while maintaining high ionic conductivity. The composition of the electrolytes determines the system's energy performance (cell voltage, allowable current densities), while the volumes determine the battery's capacity.

One of the most important characteristics of a battery is operational stability over a technically and economically viable period. Since the energy performance of flow energy storage systems depends on the electrolyte composition, an imbalance in this composition leads to accelerated degradation of the entire system.

One factor contributing to system imbalance is the phenomenon of osmosis, which occurs in systems with liquid electrolytes separated by a semipermeable membrane. The osmotic pressure in the system is determined by the osmotic pressures of electrolyte A and electrolyte B. The osmotic pressure is calculated using the Jacobus van 't Hoff equation:

$$\pi = iCRT \quad (1)$$

Where:

π – osmotic pressure;

I – isotonic coefficient;

C — molar concentration of the solution component;

R — universal gas constant;

T — temperature of the solution.

For systems using Nafion® proton-conductive (cation-conductive) polymer membranes, the mechanism of ion transport through the membrane has been investigated, including the relay mechanism and the Grotthuss-type mechanism [3]. This means that not only solvated protons in the form of hydronium ions can pass through the membrane, but also water molecules, explaining the possibility of solvent transfer from a less concentrated to a more concentrated solution. The intensity of the transfer is determined by the osmotic pressure gradient of the electrolytes; the greater the gradient, the more intense the process aimed at balancing the system.

In heterophase systems, where during charging the working ions of one of the electrolytes are reduced to an oxidation state of 0 (e.g., iron-iron, zinc-iron systems), while the second electrolyte is homophase (i.e., the working ions change their oxidation state but remain in solution without a phase transition),

the process is more complex. For example, in the iron-iron system, a reversible reaction occurs in electrolyte A:



During battery charging, Fe^{2+} ions are oxidized to Fe^{3+} , and during discharge, they are reduced back to their original concentration. In electrolyte B, the reversible reaction is:



During battery charging, Fe^{2+} ions are reduced to iron metal, which is deposited on the porous electrode. During discharge, the metal oxidizes, returning to its ionic form. In this case, one of the electrolytes becomes significantly depleted of ions during charging, lowering its osmotic pressure.

A change in the osmotic pressure of one electrolyte leads to an increased osmotic pressure gradient, intensifying solvent transfer from one electrolyte to another in an attempt to balance the system. During discharge in electrolyte B, when ions return to the solution from the solid phase but the solvent quantity has already changed, the concentration of working ions also shifts, making it impossible to return the system to its original state. These concentration changes affect the potentials of redox reactions, side processes, and current yields, leading to the degradation of the system's energy performance.

To mitigate the effects of osmosis, several possible solutions can be considered for further investigation:

1. Based on the van 't Hoff equation, adjust the system by varying the temperatures of the electrolytes. However, this approach is difficult to implement, as the electrolytes are in constant contact through the membrane, causing their temperatures to average out. Continuously cooling one electrolyte while heating the other would be energy-inefficient

2. Since osmotic pressure is physically a form of pressure, a compensation mechanism could be implemented through the design of the electrode chamber and variable electrolyte pumping modes to increase or decrease the pressure in the chamber depending on the battery cycle phase.

3. Use electrolytes with a pendulum gradient of osmotic pressure, where at the start of charging, the osmotic pressure of electrolyte B is greater than that of electrolyte A, and by the end of the process, it becomes lower. To achieve this, it is necessary to determine the isotonic coefficients of the ions comprising the electrolytes, which requires the development of techniques for measuring isotonic coefficients in high-concentration multicomponent solutions.

References

[1] European Commission. (2022). *Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions: REPowerEU Plan*. Brussels, 18.5.2022, COM (2022) 230 final

[2] Amirante, R., Cassone, E., Distaso, E., & Tamburrano, P. (2017). Overview on recent developments in energy storage: Mechanical, electrochemical and hydrogen technologies. *Energy Conversion and Management*, 372-387. <https://doi.org/10.1016/j.enconman.2016.11.046>

[3] Wang, M., Wang, L., Deng, N., Wang, X., Xiang, H., Cheng, B., & Kang, W. (2021). Electrospun multi-scale nanofiber network: Hierarchical proton-conducting channels in Nafion composite proton exchange membranes. *Cellulose*. <https://doi.org/10.1007/s10570-021-03843-5>.