**Energy from pH and salinity gradients: An experimental study of an Acid/Base battery**

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**Highlights**

* A novel flow battery, based on pH and salinity gradients, is presented.
* Ion exchange membrane parameters are estimated by electrochemical measurements.
* The performances of the device are promising for an efficient electrical energy storage.

**1. Introduction**

Electrodialysis (ED) and Reverse Electrodialysis (RED) are processes based on the selective transport of ions through ion exchange membranes (IEMs). The former, in which electrical energy is used to desalinate brackish water to produce fresh water, is one of the most valuable alternative to the common membrane desalination processes. The latter is used to produce electrical energy by directly converting salinity gradient energy. The combination of RED and ED processes leads to an electrical energy storage system [1], i.e. a concentration gradient flow battery that converts electrical energy into salinity gradients (charge phase) and recovers the energy exploiting the salinity gradient (discharge phase).

A higher energy density can be obtained using both salinity and pH gradients. This new technology is called Acid/Base Flow Battery (AB-FB) where bipolar membranes (BPMs) and typical IEMs are used to obtain acid and base streams during the charge phase and to produce electrical energy from electrolytes with different pH and salinity during the discharge phase. The use of hydrochloric acid and sodium hydroxide solutions (1 M) leads to an electromotive force (EMF) over the BPM of 0.83 V, one order of magnitude larger than the EMF that can be extracted from salinity gradients [2].

In the present work the performances of this new AB-FB were studied by changing operating conditions such as feed solutions composition and number of repeating units. Electrochemical measurements have been also carried out to study monopolar membranes properties.

**2. Methods**

A lab-scale setup (provided by Fumatech, Germany) equipped with a variable number of triplets (Acid/Base battery repeating unit) with a membrane active area of 10 x 10 cm2 was used for the experimental campaign. The triplet was composed by a cation exchange membrane (CEM), an anion exchange membrane (AEM) and a BPM, each one separated from the adjacent by a spacer 500 m thick. Two DSA electrodes were used in the end-compartments to convert ionic fluxes into electric fluxes. A cross-flow arrangement was adopted for feeding solutions that were prepared by using demineralized water and NaCl, HCl and NaOH. The aqueous electrode rinse solution was 0.25 M in Na2SO4. The performances of the AB-FB have been experimentally studied under different charge and discharge conditions with different acid and base concentrations.

Electrochemical measurements (among these, Electrochemical Impedance Spectroscopy, EIS, was used) have been carried out in order to investigate the effect of electrolytes composition on membranes permselectivity, membrane and interface resistances of the monopolar membranes.

**3. Results and discussion**

Open Circuit Voltage (OCV) values of the device were recorded by changing the concentration of acid and base aqueous solutions (reaching 1 M). These solutions were mixed with NaCl in order to reduce the concentration gradient of NaCl over the monopolar membranes. During the discharge phase, too high current density values can lead to delamination of bipolar membranes with consequent device failure. At high number of triplets, part of the electrical energy generated can be dissipated due to the onset of parasitic currents inside the stack. Charge-discharge flow battery cycles have been also studied starting from “pure” NaCl solutions (beginning of charge phase), then estimating round-trip efficiency of the system as function of operating conditions.

Membranes resistance were estimated by data fitting (with an appropriate electric equivalent circuit) of the electrochemical impedance spectra recorded by changing solution compositions and flow velocity. Membrane resistance was not so influenced from flow velocity whilst values of boundary layer resistance changes by changing the hydrodynamic conditions.

**4. Conclusions**

A novel flow battery based on pH and salinity gradients is presented. Feeding more concentrated acid and base solutions leads to an increase of the obtainable energy from the device, although at high number of triplets part of the generated energy is dissipated in parasitic currents. During discharge phase, too high current density values cannot be reached due to possible delamination phenomena of bipolar membranes. Membranes characteristics were estimated by electrochemical measurements and they could be used as input in system modelling activity. Further experimental studies are necessary to improve the efficiency of the system.

**References**

1. W.J. van Egmond et al., J. Power Sources 325 (2016) 129–139.
2. W.J. van Egmond et al., Int. J. Energy Res. 42 (2018) 1524-1535.

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