

## Application of electro dialysis to the production of Vitamin C

Lixin Yu\*, Aiguang Lin, Liping Zhang, Cuixian Chen, Weijun Jiang

Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

Received 9 December 1998; received in revised form 21 June 1999; accepted 5 December 1999

### Abstract

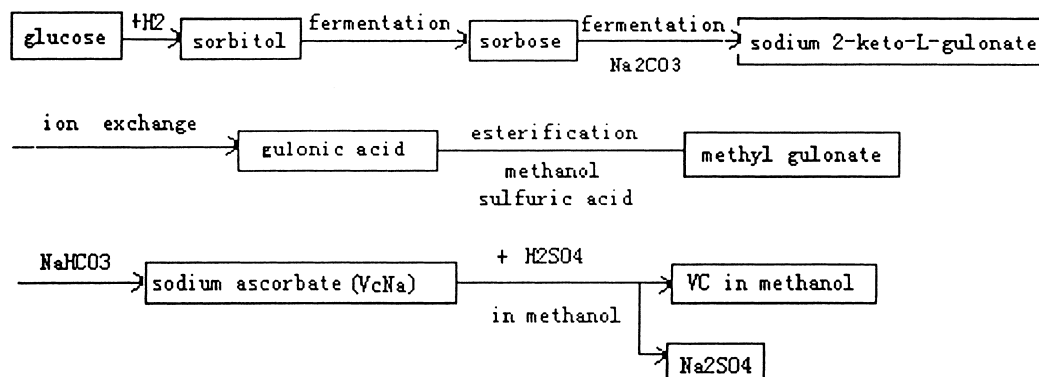
Bipolar **membrane** electro dialysis is applied to the acidification of sodium 2-keto-L-gulonate and sodium L-ascorbate to replace the original ion exchange acidification for sodium gulonate, and sulfuric acidification for sodium L-ascorbate in the production of Vitamin C. Technical feasibility and current efficiency is studied. Ordinary electro dialysis is applied to the removal of sodium sulfate in the final Vitamin C solution. Sodium sulfate can be effectively removed with little Vitamin C loss. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* L-ascorbic acid (Vitamin C); 2-keto-L-gulonic acid; Bipolar membrane; Electro dialysis; Desalination

### 1. Introduction

In one of the conventional production processes of Vitamin C there are two steps which relate to the conversion of salts to their corresponding acids.

Bipolar membrane electro dialysis [1–3] can be used to replace the two acidification processes mentioned above. By using this method, the ion exchange column for the acidification of sodium gulonate and the regeneration process of



In the step of acidification of sodium 2-keto-L-gulonate, an ion exchange method is commonly used. Large ion exchange columns are employed and batch operation has to be used for the regeneration of ion exchange resins. In the conversion of sodium ascorbate to Vitamin C, sulfuric acid is added to the methanol solution of sodium L-ascorbate to form Vitamin C, which is soluble in methanol, and sodium sulfate, which can be removed from the reaction system according to its low solubility in methanol. Vitamin C is obtained after methanol is evaporated.

resins can be omitted. So the process can be simplified and the acid for the regeneration of resins can also be saved. In the case of the acidification of sodium ascorbate, when bipolar membrane electro dialysis is employed, the conversion process can be conducted in aqueous solution. Methanol and sulfuric acid can therefore be saved.

The final Vitamin C solution may contain some sodium sulfate, which is introduced to the mixture in the upstream operation where sulfuric acid is used as catalyst. If  $\text{SO}_4^{2-}$  is not removed from the solution, the purity of product Vitamin C will not be guaranteed. The salt can be removed by means of ordinary electro dialysis with little Vitamin C loss.

\* Corresponding author. Tel.: +86-10-62785504; fax: +86-10-62770304. E-mail addresses: yulixin@263.net, yulixin@mail.tsinghua.edu.cn (L. Yu)

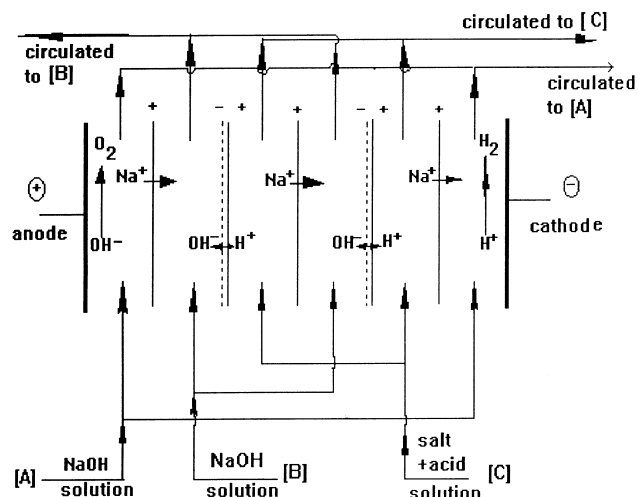


Fig. 1. Scheme of the bipolar membrane electro dialysis conversion of salt (NaR) to acid (HR).

## 2. Experimental

The bipolar membrane electro dialysis scheme for the acidification process is shown in Fig. 1.

Hydrogen ions, which are generated from water splitting in the bipolar membranes under the applied electric field, go into the acid cells and combine with the R groups to form weak acid HR (either ascorbic acid or gulonic acid). Sodium ions from the original salt go through the cation exchange membranes to the alkali cells and combine with the hydroxyl groups from the bipolar membranes. Bipolar membranes used in this study include BP-1 membranes provided by Graver Co., USA, heterogeneous bipolar membranes from Shanghai Chemical Factory and bipolar membranes made in our lab. The best results come from BP-1 membranes. Cation exchange membranes are provided by Shanghai Atomic Nucleus Institute.

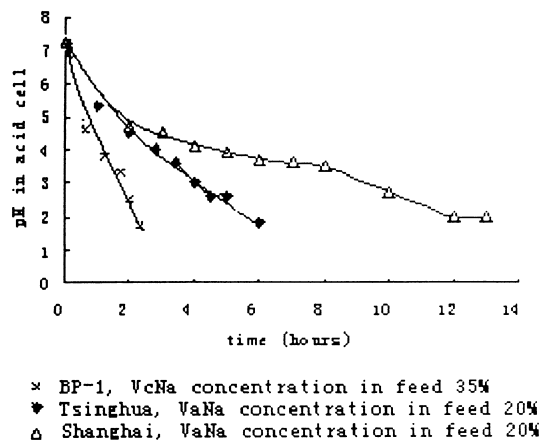


Fig. 2. pH change during the bipolar membrane electro dialysis conversion of sodium ascorbate.

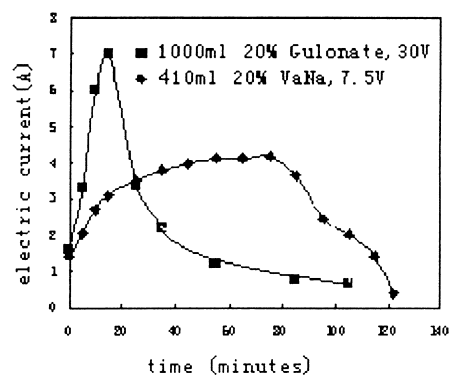


Fig. 3. Electric current vs. conversion ratio for sodium ascorbate and gulonate.

The membrane size in electro dialysis stack is 0.1 m in width and 0.2 m in length with an effective area of 0.0098 m<sup>2</sup>. The spacer between membranes is 1.8 mm thick.

The salt solution ranges from 350 to 1000 ml in each batch of experiment and the NaOH in the alkali cell is 500 ml with an initial molar concentration of 0.5 M.

During the experiment the voltage is kept constant. After the pH of the acid cell solution and the electric current versus time are measured, the conversion ratio and the current efficiency can be calculated. The conversion ratio can be calculated on the basis of the electrolytic dissociation equilibrium between the generated weak acid (both Vitamin C and gulonic acid are weak acids), H<sup>+</sup> ions and total R<sup>-</sup> in the solution. But this is somewhat approximate, because the volume of the solution might change to some degree during the experiment.

The final Vitamin C product is obtained after vacuum evaporation of the aqueous solution after electro dialysis treatment, and the quality of the Vitamin C product is analyzed by North East Pharmaceutical Company, Shengyang, Liaonin Province, PR China.

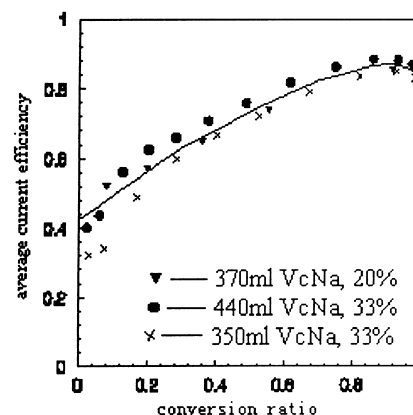


Fig. 4. Average current efficiency vs. conversion ratio for sodium ascorbate.

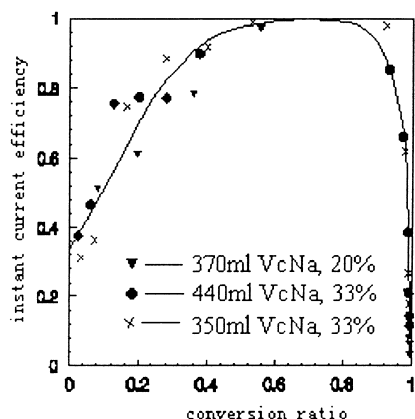


Fig. 5. Instant current efficiency vs. conversion ratio for sodium ascorbate.

### 3. Result

#### 3.1. Electric current change and pH change during the conversion process

The final pH value of the solution in acid cell relates to the conversion ratio. So pH data are recorded during the experiment to monitor the conversion process, and pH changes during the experiments are shown in Fig. 2.

At constant voltage, the current goes up at the beginning and then goes down continuously, as shown in Fig. 3. The initial increase of current is the result of temperature rise of the solution. Generally, we start the experiment at 25°C and the temperature changes gradually to 35°C and then stays unchanged. The subsequent decrease of electric current is the result of the Na<sup>+</sup> decrease in the solution, which leads to high electric resistance of the acid cell solution.

#### 3.2. Current efficiency

Average current efficiency ( $\eta$ ) is defined as the ratio of electricity theoretically needed for the conversion ( $Q_c$ ) to the total electricity input into the electro dialysis module ( $Q$ ).

$$\eta = \frac{Q_c}{Q} \quad (1)$$

$$Q_c = mF \quad (2)$$

$$Q = nIt \quad (3)$$

where  $m$  is the mole of acid produced from the beginning to time  $t$ ,  $F$  the Faraday constant=96 500 C/mol,  $n$  the number of cell units, and  $I$  is the average current from the beginning to time  $t$ .

Instant current efficiency is defined as the average current efficiency during time range  $t$  to  $t+\Delta t$  as  $\Delta t$  reaches 0.

As shown in Figs. 4 and 5, the average and instant current efficiency can be as high as 90%. But as the conversion ratio goes beyond 85%, the efficiency becomes lower and lower. This is because of the decrease of the amount ratio of Na<sup>+</sup> to H<sup>+</sup>. At high conversion ratio, the content of Na<sup>+</sup> is less in the solution; so more H<sup>+</sup> will go through the cation exchange membranes into the alkali cells, leading to the decrease of current efficiency. But we are puzzled by the increasing part of the curves in Figs. 4 and 5, though a lot of experiments show the same trend. More attention should be paid to the analysis of this phenomena in the further study on this subject.

The decline in current efficiency will finally increase the electricity consumption for a certain amount of conversion. Theoretically the current efficiency will approach zero at 100% conversion ratio. So a balance has to be found in choosing the terminal pH in the conversion experiment, at which the purity of final Vitamin C product can be guaranteed and the electricity consumption is acceptable. Table 1 gives some experimental conditions and quality analysis results of the final Vitamin C products.

#### 3.3. Ordinary electro dialysis result for the removal of SO<sub>4</sub><sup>2-</sup>

As mentioned above, some SO<sub>4</sub><sup>2-</sup> has been introduced into the conversion system in the upstream operation. Qualified Vitamin C product can be obtained from the bipolar membrane electro dialysis conversion solution through partial concentration under vacuum and crystallization at cool temperature (around 4°C). But the amount of SO<sub>4</sub><sup>2-</sup> in the remaining solution after crystallization will be higher. If not

Table 1  
Some experimental conditions and final Vitamin C quality analysis results

No.	Source of bipolar membrane	Sodium ascorbate content in feed (wt.%)	Terminal pH value of acid cell solution	Vitamin C content in final product (wt.%)	Na <sup>+</sup> content in final product (wt.%)	SO <sub>4</sub> <sup>2-</sup> content in final product (wt.%)
1	Shanghai	20	2.25	99.1	0	0
2	Shanghai	20	2.25	98.7	0.44	0
3	Tsinghua	20	1.36	98.3	0	0.1
4	Tsinghua	30	1.42	99.8	0	0
5	Tsinghua	20	1.76	98.7	0.28	0.05
6	USA BP-1	20	2.3	98.7	0.82	0
7	USA BP-1	35	1.71	98.7	0.22	0

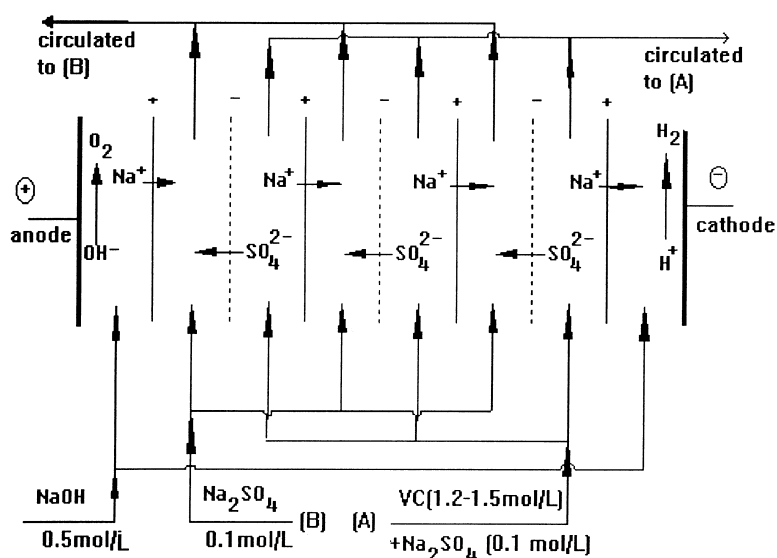
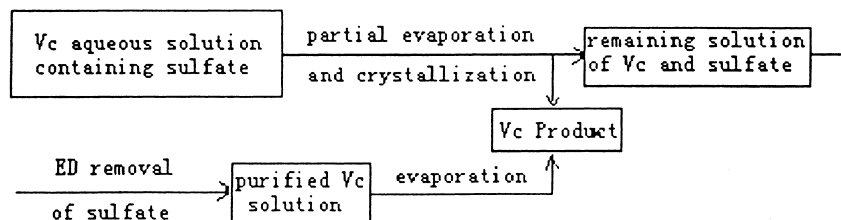


Fig. 6. Scheme of ordinary electro dialysis for the removal of sodium sulfate from Vitamin C solution.

removed, the  $\text{SO}_4^{2-}$  will affect the purity of the Vitamin C product from the remaining solution after further vacuum evaporation and crystallization.

solution,  $\text{H}^+$  and  $\text{Vc}^-$  will also go through the cation and anion exchange membranes, respectively, leading to a loss of Vitamin C. The experiment shows that  $\text{SO}_4^{2-}$  can be



An ordinary electro dialysis system consisting of cation and anion exchange membranes is employed to achieve the goal of  $\text{SO}_4^{2-}$  removal (see Fig. 6). When using ordinary electro dialysis to remove  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  from Vitamin C

effectively removed with little Vitamin C loss (Fig. 7). But when we pursue complete  $\text{SO}_4^{2-}$  removal (corresponding to low  $\text{SO}_4^{2-}/\text{Vc}^-$  ratio), we will lose more Vitamin C.

The reason for the good removal results can be explained from two aspects. One is that Vitamin C is a relatively weak acid and few  $\text{H}^+$  and  $\text{R}^-$  exist in the solution. The other is that  $\text{SO}_4^{2-}$ , smaller in size than  $\text{R}^-$  and having double electric charge, will go faster and easier than  $\text{R}^-$  through the anion exchange membrane.

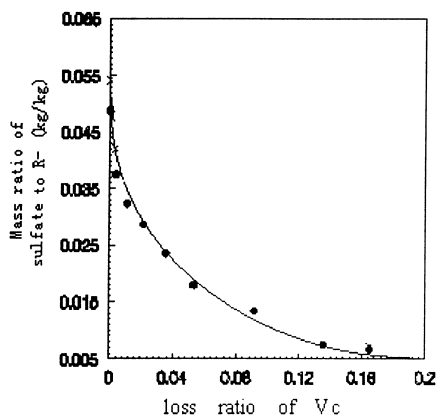


Fig. 7.  $\text{SO}_4^{2-}$  removal ratio vs. Vitamin C loss.

#### 4. Conclusions

Bipolar membrane electro dialysis can be applied to the acidification processes of sodium L-ascorbate and sodium 2-keto-L-gulonate to replace the original sulfuric acidification process and ion exchange method in Vitamin C production process. At above 98% conversion ratio the average current efficiency is about 70%. The electricity consumption for the electro dialytic conversion of 1 kg of Vitamin C or gulonic acid is about 1 kWh.

Ordinary electro dialysis can be used to remove  $\text{Na}_2\text{SO}_4$  from Vitamin C solution with little Vitamin C loss.

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