

CONTINUOUS ELECTRODEIONIZATION PROCESSES FOR PRODUCTION OF ULTRAPURE WATER

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ABSTRACT

Continuous electrodeionization (CEDI) is a technology that utilizes ion exchange membranes, ion exchange media (typically ion exchange resins), and a DC electric potential to remove ionic impurities.

This paper will review the technology and its applications in the microelectronics industry. Results are presented for a new process that can produce water with high resistivity and ultra-low levels of dissolved ions such as silica and boron.

INTRODUCTION

Continuous electrodeionization (CEDI) is a technology that is increasingly being used for production of deionized water in industries such as microelectronics, power generation and pharmaceuticals

Most commercially available CEDI devices comprise alternating cation- and anion-exchange membranes, separated by spacers which contain flow compartments with inlets and outlets. A transverse DC electrical field is applied by an external power source using electrodes at the bounds of the membranes and compartments. The compartments bound by an anion membrane facing the anode and a cation membrane facing the cathode are diluting compartments. The compartments bound by an anion membrane facing the cathode and a cation membrane facing the anode are concentrating compartments. The ideal ion exchange membrane is permeable only to the ions of a specific polarity and not to water. To facilitate ion transfer in low ionic strength solutions, the diluting compartments are filled with ion exchange resins. In some versions the concentrating compartments are also filled with resins

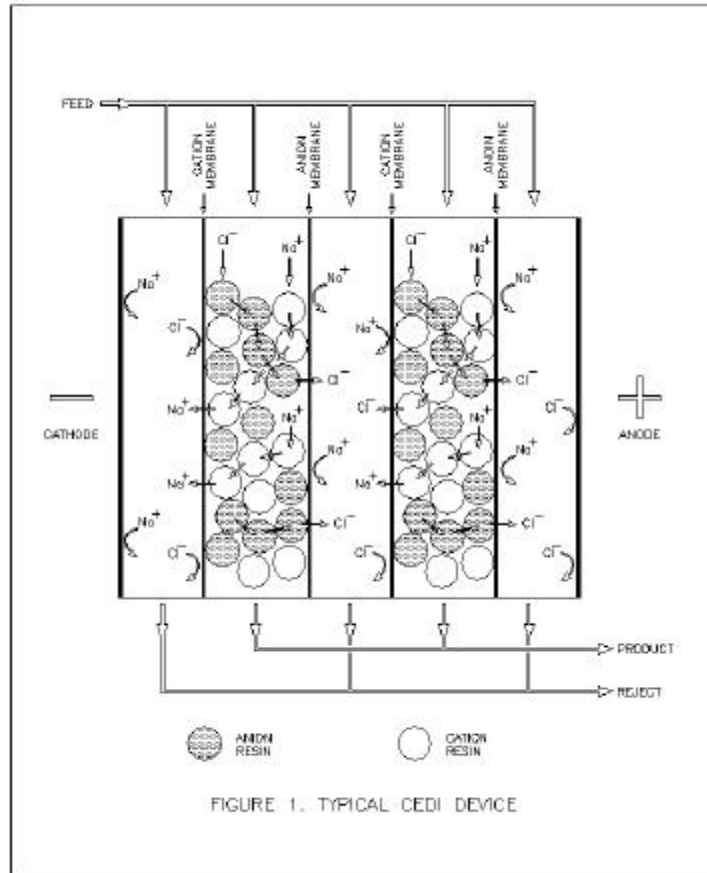


Figure 1 illustrates the removal of ions in a CEDI device. Cations in the feed water to the diluting compartments are adsorbed onto the cation exchange resins and are transported under the applied electric field towards the cathode. Once a cation passes through the cation membrane into the adjacent concentrating compartment, its progress is blocked by the anion membrane on the other side of the compartment. The converse applies to the anions. The result is that the diluting compartments are depleted of ions and the concentrating compartments are concentrated with ions.

CEDI devices are available in either plate and frame design, similar to a filter press, or spiral wound design. In this paper we will limit our discussion to the more common plate and frame devices, in which alternating flat diluting and concentrating cells are stacked between the electrodes and sandwiched together with some type of closing mechanism. Increasing the number of cell pairs (one dilute and one concentrate cell) increases the capacity of the unit.

Plate and frame devices can be broken down into two major subsets: thin cell and thick cell, based on the thickness of the diluting compartments. For the purposes of this paper, thin cell devices have diluting cell thickness of 2-3 mm, vs. 8-10 mm for the thick cell.

THIN CELL CEDI

CEDI devices with thin cells are well established in the market. An example is the CDI™ (continuous deionization) product line from U. S. Filter, which was first commercialized in 1987 [1]. The diluting compartment for these devices is typically filled with mixed ion exchange resins. The concentrating compartments are filled with an inert mesh, which separate the membranes and improve flow distribution.

In the production of ultrapure water, the feed to a CEDI device is pretreated with reverse osmosis. This water contains low amounts of dissolved, ionized solids (in the range of 10 ppm as CaCO₃ or less) and some weakly ionized substances such as carbon dioxide, silica, boron, and slightly polar organics.

Ions are removed by two different mechanisms in a thin cell, mixed bed CEDI device. In a dilute solution, the concentration of mobile ions, and therefore the ionic conductance, is much higher in the ion exchange resins than in the bulk solution. Strongly ionized substances are removed first in the top portion of the bed, with the ion exchange resin simply acting as a conductor to speed the passage of ions from the dilute compartment through the respective membrane, and into the concentrating compartment. This removal mechanism is shown in Figure 1 and is referred to as enhanced transport.

As the concentration of strongly ionized substances in the bulk solution is depleted, the electric field (voltage gradient) at the interfaces between anion and cation resins or between resins and membranes of different polarity can become large enough that water splitting occurs. The resulting H⁺ and OH⁻ ions convert and maintain the resins in the regenerated state where weakly ionized substances can react, become ionized and be moved into the concentrating stream. This removal mechanism is referred to as electro-regeneration [2].

The properties of ion exchange resins and membranes can be optimized for removal of ionic species of interest. For example, the use of low cross-linked, high water content anion resins and

membranes can dramatically improve silica removal by increasing the intra-particle diffusion rate. This has been in practice for thin cell CEDI devices for several years [3].

Water splitting is critical for the removal of weakly ionized species like silica, carbon dioxide, and boron. From Faraday's law, current is a direct indication of ionic transport rate through the membrane. The amount of current above that needed for ionic transport is used primarily to move the H^+ and OH^- ions and is indicative of the amount of water splitting (neglecting other inefficiencies).

Increasing the current requires increasing the voltage and/or lowering the module electrical resistance. Increasing the voltage imparts several drawbacks including increased safety risks and decreased reliability. Efforts to reduce the overall module resistance have focused on:

1. Development of strongly acidic and strongly basic ion exchange membranes that can catalyze the water splitting reaction [4] and improve weak ion removal.
2. Reduction of the resistance of the concentrating stream.

With ion exchange resin in the diluting cell and inert screen in the concentrating cells, the concentrating stream becomes the limiting resistance in a module. Several methods have been developed to reducing that resistance:

1. Recirculation of the concentrate stream in a feed and bleed configuration, which increases the concentration and therefore the conductivity of the concentrate stream. In addition, the overall water recovery is increased. By increasing the velocity of the stream, boundary layer film thickness is reduced on the concentrate side of the ion exchange membranes, especially important when treating high salinity feed waters.

Concentrate recirculation requires the use of a pump and additional ancillary equipment for control such as motor starters and throttling valves. This adds complexity to the system design and increases overall cost. In systems with fluctuating operating conditions, operation or adjustment of the pump can make the process more labor intensive. The power required to operate the pump can be a significant portion of the total power consumption of the system. In a typical scenario, an industrial thin-cell CEDI system consumes about 1 kilowatt-hour per thousand gallons of product water (KWh/kgal), with two-thirds of that for the pump.

2. Addition of ion exchange resin to the concentrate compartment [5]. This change nearly halved module resistance and allowed a doubling of throughput at the same level of deionization. Addition of resin not only improved the overall electrical resistance but also reduced boundary layer film thickness by providing a path for transport away from the concentrate side of the membrane.
3. Injection of a salt solution into the concentrate stream. This approach has the disadvantages of introducing a chemical into the deionization process and producing a reject stream with high salinity that may prevent its recycle or reuse. The high salinity also facilitates back diffusion of ions from the concentrate to the dilute if the membranes are not ideally selective, and increases the possibility of salt bridging and electrical shorting if there is an external leakage.

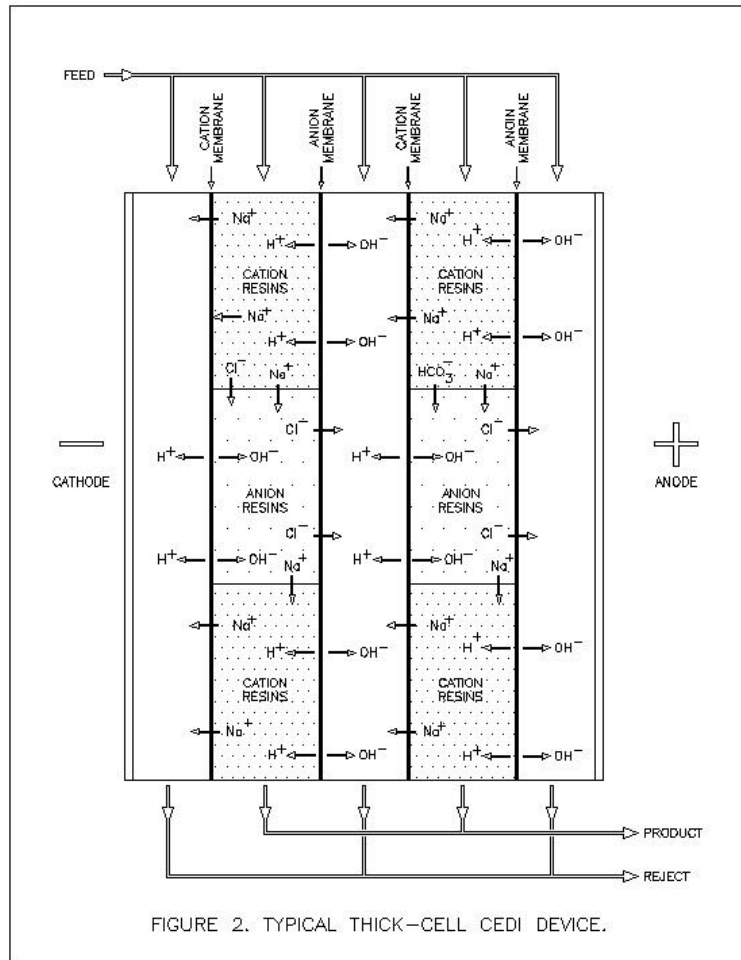
Most commercial thin-cell systems today incorporate one or more of the above approaches to reducing module resistance. Current CDI™ systems, for example, use resin filled concentrate compartments and concentrate recirculation to improve performance.

THICK-CELL CEDI

Transport of ions through the resin bed in the diluting compartment requires continuous paths of resins of the same polarity. The probability that such paths exist from one side of the compartment to the other in a mixed bed decreases as the cell thickness increases. Water splitting can still occur at dissimilar resin/resin and resin/membrane interfaces, but much of the H^+ and OH^- ions will recombine when they encounter the counter ions travelling in the opposite direction. In one study, the performance of one thick cell mixed bed device was found to be inferior to two thick cell separate bed devices [6].

The majority of thick cell CEDI devices therefore do not use mixed beds. Instead, separate layers or zones of resins of one polarity span the distance from one membrane to another (see Figure 2). In each layer or zone, the transport of ions of only one polarity is enhanced. For example, in the layers of anion exchange resins, the transport rate of anions is much higher than that of the cations. Depletion of anions at the interface between anion resin and adjacent cation membrane will cause water splitting to occur at the interface. The resulting OH^- ions replace the anions removed and maintain current. The OH^- ions also regenerate the anion resins, and the

increased pH results in dissociation of weak acids such as H_2CO_3 and H_2SiO_2 , and enhances their removal as anions. The converse occurs in a layer of cation resins. The pH in a layered device therefore alternates from basic in the anion layers to acidic in the cation layers. Ions of alternating polarity are removed as the water flows through the layers. In a thick cell CEDI device, water splitting is critical for removal of both weak *and* strong ions.



CLUSTERED BED

Thick cell CEDI devices were commercialized in 1996 by E-Cell Corporation when the first pilot units were installed [7]. These are of the clustered-bed configuration, where the cation resins are in cylindrical plugs surrounded by anion resins [8]. The axes of the cylinders are perpendicular to the membranes, and the plugs therefore form zones of cation resins that span the distance from

one membrane to the other. In order to fill the cell with the clusters, an inert binder was used to hold the resin in place. The concentrate cells were filled with open screens. To lower the resistance, continuous injection of a sodium chloride solution into the concentrate stream is a common practice in the application of this design.

LAYERED BED

Thick cell devices with the layered beds of resins in the diluting compartments were first piloted in 1995 and commercialized by U.S. Filter in 2000 as the CDI-LX™ product line. The composition and type of resins in the layers, as shown in Figure 4, can be selected to enhance removal of specific ions. The concentrating compartments are thinner than the diluting compartments and are filled with cation resins to reduce the electrical resistance.

Typical performance of a CDI-LX module is shown in Table A. The feedwater was softened and treated by single pass reverse osmosis. The results show the effects of temperature and current on product resistivity and silica removal. Temperature affects the rate of water splitting and diffusion of ions through the resins, both of which are critical to performance of thick-cell CEDI devices.

Table A. Effect of temperature and current on performance of thick-cell CEDI device

| | Feed Temperature 17°C | | Feed Temperature 10°C | |
|-----------------------------|-----------------------|-------|-----------------------|-------|
| Feed Conductivity (µS/cm) | 6.61 | 6.51 | 6.45 | 5.94 |
| Feed CO ₂ (ppm) | 1.88 | 1.88 | 1.88 | 1.88 |
| Feed Silica (ppb) | 313.5 | 326.5 | 315.5 | 249.5 |
| Product Resistivity (MΩ-cm) | 16.2 | 17.2 | 14.3 | 16.3 |
| Product Silica (ppb) | 13.5 | 3.5 | 27.5 | 6.5 |
| Product Silica removal (%) | 95.7 | 98.9 | 91.3 | 97.4 |
| Current (Amps) | 3.21 | 6.01 | 3.22 | 5.99 |

MECHANICAL ADVANTAGES OF THE THICK CELL DESIGN

In a thin cell device, sealing between the membranes and the spacers is usually achieved by using flexible membranes as gaskets or by bonding the membranes to the spacers with adhesives

or by thermal welding. Thermal bonding requires spacer materials that have similar melting temperature to the membranes, such as polyethylene. Thin cell devices are typically designed for operating pressure of 40-60 psig.

In the CDI-LX modules, the thicker spacers in thick-cell devices allow for O-ring seals, which can increase operating pressure to over 100 psig at temperature above 45°C, with zero leakage. The spacer material can be chosen purely for its mechanical and thermal properties. Engineering plastics now available can allow heat sanitization to 80°C, thereby eliminating the requirement for chemical sanitization in the event of bacterial fouling in the water system. Recent tests have shown that a thick-cell layered bed device can be hot water sanitized 156 times, corresponding to one cycle every week for three years, with no degradation in module performance.

APPLICATION TO MICROELECTRONICS

The combination of reverse osmosis and continuous electrodeionization provides a chemical-free alternative to conventional ion exchange demineralization. This hybrid process has been widely used in producing pharmaceutical-grade water, and is becoming more common in the production of ultrapure water for power plants and for microelectronics manufacturing. In this section we will summarize the performance of several CEDI installations.

MATSUSHITA DENSHI (NATIONAL/PANASONIC) IN SINGAPORE

A new water treatment system was installed in 1997 at this factory to replace the original chemically regenerated mixed bed deionizers [9]. The system incorporated three main demineralization technologies: single pass reverse osmosis (RO) for bulk, or roughing demineralization, continuous electrodeionization (CEDI) for makeup demineralization, and mixed bed bottles for final polishing. By employing CEDI and non-regenerable mixed bed polishers, the use of acid and caustic for the DI water system was completely eliminated.

Water from the raw water tank is pretreated by a multi-media filter and a granular activated carbon filter. A polyacrylic acid type antiscalant is injected to prevent formation of mineral deposits on the RO membranes, and bisulfite is injected to provide additional assurance that the thin film composite polyamide RO membranes are never exposed to an oxidant such as chlorine. The RO feed water is then further pretreated by 1-micron cartridge filtration. The RO system

operates at about 75% water recovery and operates in start/stop mode based on the level of water in the RO product tank.

The continuous electrodeionization system consists of a single plate-and-frame CDI™ module with 240 product compartments. This device is of the thin-cell design, using mixed-bed ion exchange resin filler in the dilute compartments and gasketed screen-type spacers in the concentrate compartments. This CDI system includes a concentrate recirculation pump to allow operation at about 90% water recovery. Unlike the RO system, the CDI system operates continuously, always feeding water into the nitrogen-blanketed DI tank. This maintains high CDI product resistivity and minimizes the possibility of bacterial growth, due to the bacteriostatic effect of the electric field. If the DI tank fills up, it will then overflow back to the RO product tank. PVC piping is used through the pretreatment, RO and CEDI systems and into the DI water tank.

Product from the CDI system is further polished by low-TOC mixed bed polishers, 1-micron cartridge filters, disinfecting UV, and 0.2-micron final filters. Polypropylene (PP) piping is used for these polishing loops.

The RO/CDI system was commissioned in July 1997 and has now been operating successfully for over three years. Operation of the plant has met expectations in terms of reliability and on-line performance, and has consistently met the contract specification for final product water quality. In addition, the manufacturing facility achieved ISO 14001 certification in December 1997.

Over the past three years, the CDI product water quality has stayed fairly constant at 15 - 16 mΩ-cm in spite of decrease in RO performance, and the polishing mixed beds have consistently produced 18 mΩ-cm. The CDI flow rates and pressure drops have also remained relatively stable throughout the three years of operation, an indication that there has not been significant scaling or fouling of the CDI module.

The final product water for this system has periodically been sent to an outside laboratory for analysis. Some of these results are given in Table B, and they show that the RO/CDI system produces higher quality water than did the old mixed bed demineralizer system.

Table B: Analysis of deionized water

| | April 1997 Original mixed bed system | July 2000 RO/CDI system |
|-----------------|---|----------------------------|
| Sodium, ppb | 0.1 | Below detection level |
| Silica, ppb | 15 | 2 |
| TOC, ppb | 132 | 5 |
| TCC, cfu/100 mL | 106 | <1 |

Overall the RO/CDI system has resulted in 37-46% annual savings in operating costs relative to the conventional DI system.

450 GPM (100 M³/HR) MAKEUP DI SYSTEM

This system provides makeup DI water for semiconductor wafer fabrication. Deionization is accomplished by two-pass RO, followed by CEDI and non-regenerable mixed bed DI. The CEDI modules are of thin cell design.

The installation has been in operation for over 6 years. The CEDI product typically contains less than 5 ppb silica and TOC, with resistivity greater than 16 mΩ-cm. The product is of high enough quality that the life of the mixed bed resins is generally over 1 year [9].

70 GPM (16 M³/HR) DI WATER RECLAIM

This system was installed to reclaim back grind wastewater. The wastewater is first pretreated by microfiltration, and then deionized with a thin-cell CEDI system with resin filling in both the dilute and concentrate compartments. The system has been in continuous operation for over 4 years, with typical CEDI performance of over 17 mΩ-cm product water resistivity and greater than 99.7% removal of most ions (see Table C) [9].

Table C. Performance of CDI system for reclaiming DI water (all concentrations are in ppb)

| Solute | % Removal | CDI Feed | CDI Product |
|-----------|-----------|----------|-------------|
| Ammonium | >99.73 | 3.7 | <0.01 |
| Boron | >99.7 | 3.4 | <0.01 |
| Calcium | 99.96 | 227 | 0.1 |
| Magnesium | >99.85 | 6.5 | <0.01 |
| Nitrate | >99.96 | 54.1 | <0.02 |
| Potassium | 99.92 | 12.8 | 0.01 |
| Sodium | 99.82 | 5.46 | <0.01 |
| Chloride | 99.85 | 63.8 | 0.097 |
| Sulfate | 98.5 | 8.6 | 0.129 |
| Silica | >96.2 | 26 | <1 |

100 GPM (22 M³/HR) DI MAKEUP SYSTEM UTILIZING THICK-CELL MODULES.

A 100 gpm (22 m³/hr) CDI-LX system was installed in December, 2000 at Honeywell Solid State Electronics Center to replace a two bed demineralizer system. The primary motivation of the customer was to eliminate the chemicals needed for regeneration [10]. The pretreatment is either single pass or double pass RO, depending on the water demand. The CEDI product will be polished by mixed bed DI. Startup is planned in January 2001.

FURTHER ADVANCES IN CEDI PERFORMANCE

In all CEDI applications describes earlier, the product from the CEDI devices is further polished by mixed bed DI prior to end use or prior to introduction into a DI loop. The life of the mixed bed DI may be limited by breakthrough of the weakly ionized species such as silica and boron.

We are currently working on improving the deionization performance of the CEDI devices to minimize the ionic loading on the mixed beds and, ultimately, to eliminate the requirement for the mixed bed altogether.

Preliminary results are promising. Table D shows the results of a recent test with a thick cell layered bed system [11]. The feedwater was RO permeate with conductivity of 7 μ S/cm with 2 ppm of carbon dioxide. Samples of the RO permeate, the CEDI product, and the product water from a separate mixed bed DI system were submitted to an outside laboratory at the same time for comparison. The DI sample was from a high-purity polishing cartridge that contains specially treated resins and inert plastics. Pretreatment for the cartridge consisted of softening, reverse osmosis and chemically regenerated mixed bed ion exchange. The piping and valves on the CEDI system was of PVC material.

Over 80 different elements and ions were analyzed for. Only those detected are presented in the table. It is very interesting to note the concentration of boron in the mixed bed product, 190 ppt, whereas it was below the detection limit (DL) (<50 ppt) in the CEDI product water. The boron removal for the CEDI was greater than 99.6% and the silicon (silica) removal was greater than 99.5%.

The work is ongoing and additional results will be presented at the conference.

Table D. Water analysis for the thick-cell CEDI system configured for production of ultrapure water (all concentrations are in ppb)

| Component | RO Product | CEDI Product | Removal (%) | MB Product | Detection Limit |
|---------------|------------|--------------|-------------|------------|-----------------|
| Anions by IC | | | | | |
| Chloride | 750 | * | >99.99 | * | 0.02 |
| Nitrate | 58 | * | >99.96 | * | 0.02 |
| Phosphate | 27 | * | >99.92 | * | 0.02 |
| Sulfate | 210 | * | >99.97 | * | 0.05 |
| Cations by IC | | | | | |
| Sodium | 1100 | 0.24 | >99.97 | * | 0.01 |
| Ammonium | 7 | * | >99.28 | * | 0.05 |
| Potassium | 26 | * | >99.92 | * | 0.02 |
| Calcium | 6 | * | >99.66 | * | 0.02 |

| Trace Metals by ICP-MS | | | | | |
|------------------------|------|------|--------|------|-------|
| Aluminum | 0.22 | * | >98.63 | * | 0.003 |
| Boron | 13 | * | >99.61 | 0.19 | 0.05 |
| Lithium | 0.05 | * | >96.00 | * | 0.002 |
| Manganese | 0.03 | * | >93.33 | * | 0.002 |
| Potassium | 23 | * | >99.56 | * | 0.1 |
| Rubidium | 0.04 | * | >97.50 | * | 0.001 |
| Silicon | 110 | * | >99.54 | * | 0.5 |
| Sodium | 1300 | 0.26 | >99.98 | * | 0.007 |
| Zinc | 0.09 | * | >94.44 | * | 0.005 |

Below detection limit

SUMMARY

Continuous Electrodeionization is a proven technology for microelectronic applications. Most current applications are for production of makeup DI water, although in-line operation in a polishing loop as well as wastewater reclamation is possible. Market forces as well as competitive pressures have resulted in rapid improvement in the deionization performance and reliability, as well as reduction in cost. Compared to ion exchange demineralizers for makeup, a RO/CEDI system can produce higher quality water, reduce or eliminate the use of chemicals, and lower the operating cost.

Current development efforts at U.S. Filter are focused on development of CEDI systems that can produce ultrapure water with quality equal to or better than that from a mixed bed polisher.

BIOS

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