CHEMISTRY LETTERS, pp. 1779-1782, 1993.

Reduction of Nitrobenzene on Solid Polymer Electrolyte Composite Electrodes Using a Hydrocarbon Sulfonate Ion-Exchange Membrane[1)]

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Solid polymer electrolyte composite electrodes using a hydrocarbon sulfonate ion-exchange membrane, Selemion® CMV, were prepared (Cu-Selemion). Nitrobenzene was electroreduced on Cu-Selemion. At current densities greater than 32 mA cm^{-2}, the current efficiency for aniline production decreased significantly because of hydrogen evolution. The reaction selectivity and the mass transport rate were improved by Nafion coating on Selemion. With Nafion-modified Cu-Selemion, aniline was obtained selectively and the current efficiencies for aniline production were as high as 90 % up to 70 mA cm^{-2}.

Solid polymer electrolyte (SPE) composite electrodes have been extensively studied for use in water electrolyzers, brine electrolyzers and fuel cells. We have studied on the reduction of nitrobenzene with SPE composite electrodes using a perfluorosulfonate ion-exchange membrane, Nafion®, as SPE material.[2-4)] With the composite electrode aniline was obtained selectively with a current efficiency greater than 90%. Owing to the selective aniline production, the SPE method is promising for use in industrial aniline synthesis. However, since perfluorosulfonate membranes are generally expensive, it is desirable to use hydrocarbon sulfonate ion-exchange membranes as SPE material. In the present work SPE composite electrodes using a hydrocarbon sulfonate ion-exchange membrane, Selemion® CMV (Asahi Glass Co.), were prepared, and the reduction of nitrobenzene was investigated using the electrodes.

Selemion is a co-polymer of styrene and divinylbenzene which contains sulfonate groups as ion-exchange sites, and is reinforced with polyvinyl chloride fibers. A porous copper layer was deposited on one side of the membrane of 3.0 cm in diameter by an electroless plating method.[5)] One face of the membrane was exposed to a reductant solution (0.01 M $NaBH_4$, 1 M = 1 mol dm^{-3}), and the other face to a copper ion solution (0.1 M $CuSO_4$). A porous copper layer was deposited on the reductant-side surface of the membrane. The copper layer deposited on the Selemion membrane was stable in H_2SO_4 as long as 2 days. The resulting SPE composite electrode is referred to hereafter as Cu-Selemion.

Nafion-modified Cu-Selemion composite electrodes were prepared as follows: 0.3 cm^3 of a solution of Nafion dissolved in alcohol (Aldrich, containing 5 wt% Nafion of EW = 1100) was spread with a microsyringe onto a Selemion membrane with a diameter of 3.0 cm and air-dried to remove the solvent for 10 h. The calculated thickness of the Nafion coating is 8.5 μm. A porous copper layer was deposited on the Nafion layer by the electroless plating method described above.

The electrolytic cell was described in previous papers.[2,3] The cell was composed of two compartments, which were separated by the SPE composite electrode. The SPE composite electrode was used as cathode, and the effective geometric surface area was 3.1 cm^2. The catholyte was methanol solution containing 30 vol% nitrobenzene (6 cm^3), and the anolyte was aqueous 0.25 M H_2SO_4 (6 cm^3). A platinum wire was inserted in the anolyte and used as anode. Electrolysis was carried out galvanostatically. The total charge passed during each run was 800 coulombs. After electrolysis, the catholyte was analyzed by HPLC without pretreatment. Polarization curves were measured using an SPE electrolytic cell fitted with a Luggin capillary placed in the anode compartment.[6]

The variations of the current efficiency for aniline production and cell voltage with current density obtained with Cu-Selemion are shown in Fig. 1. The maximum current efficiency of 80% was obtained at a current density of 16 mA cm^{-2}. The current efficiency decreased significantly at current densities greater than 32 mA cm^{-2}. Gas evolution was observed in the cathode compartment at the high current densities, and hence hydrogen evolution is considered to have occurred as a side reaction. Figure 1 also shows the variations of the current efficiency for aniline production and cell voltage obtained with Cu,Pt-Nafion in the previous study.[2] The maximum current efficiency was greater than 95%, and no significant decrease in current efficiency was seen at current densities up to 100 mA cm^{-2}. The active site of SPE composite electrodes has been considered to be located inside the ion-exchange membrane,[2,3,7] that is, in the region where the membrane phase and electrode overlap.[8] Nitrobenzene must diffuse from the catholyte to the active site to receive electrons from the electrode material. Hence, the hydrogen evolution on Cu-Selemion at high current densities means insufficient mass transport of nitrobenzene from the catholyte to the active site of the electrode.

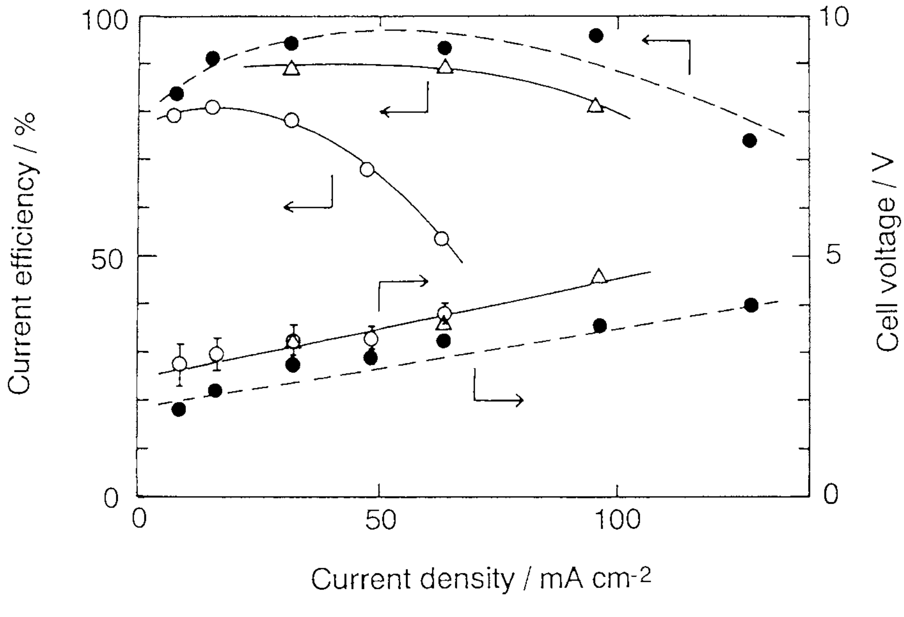

Fig. 1. Variations of current efficiencies for aniline production and cell voltages with current density obtained with (○) Cu-Selemion, (●) Cu,Pt-Nafion,[2] and (△) Nafion-modified Cu-Selemion.

Quasi-steady state polarization curves obtained at a slow sweep rate of 1.0 mV s^{-1} are shown in Fig. 2. Curves (a) and (b) were obtained with Cu-Selemion and Cu,Pt-Nafion, respectively, using 20 mM nitrobenzene in methanol as the catholyte. Curves (c) and (d) were obtained with Cu-Selemion and Cu,Pt-Nafion, respectively, using neat methanol (i.e. without added nitrobenzene) as the catholyte. On both SPE composite electrodes, cathodic current for the reduction of nitrobenzene started to flow at -200 mV *vs.* Ag/AgCl. The limiting currents are about 10 and 30 mA for Cu-Selemion and Cu,Pt-Nafion, respectively. These results indicate that the mass transport of nitrobenzene in Selemion is about three times slower than that in Nafion.

Nafion membranes are not cross-linked, and have a flexible structure.[9)] In addition, Nafion membranes swell more in many organic solvents than in water.[10)] Hence, the mass transport of nitrobenzene inside Nafion is considered to be fairly easy. On the other hand, Selemion is highly cross-linked, and has a homogeneous structure, in which the ion-exchange sites are distributed uniformly throughout the membrane. It is difficult for organic reactants, such as nitrobenzene, to diffuse through such a rigid structure of Selemion. Therefore, it seems reasonable that the mass transport in Selemion is slower than that in Nafion.

With Cu,Pt-Nafion aniline was the sole product, and no other organic by-products were detected by HPLC.[2)] On the other hand, with Cu-Selemion an organic by-product was detected with HPLC. The by-product has not been identified yet because of its high reactivity.[11)] The molecular ion peak of the mass spectrum was observed at m/z = 198, which suggests a dimer production.

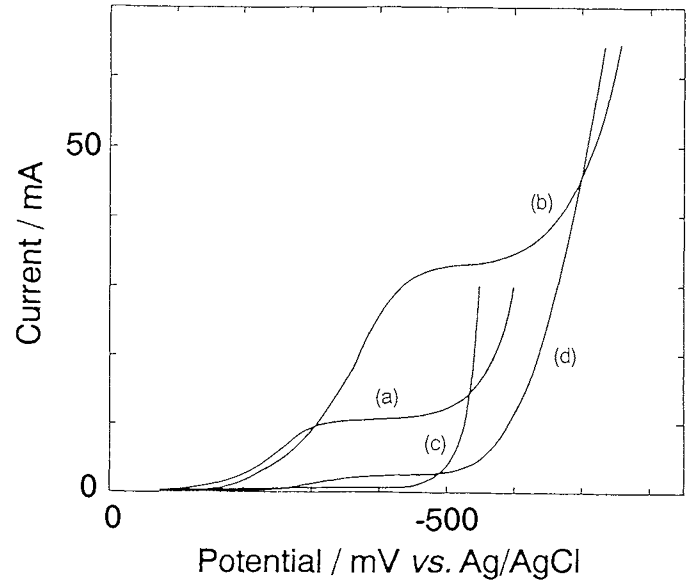

Fig. 2. Quasi-steady state polarization curves obtained at 1.0 mV s^{-1}: (a) 20 mM nitrobenzene in methanol and Cu-Selemion, (b) 20 mM nitrobenzene in methanol and Cu,Pt-Nafion, (c) methanol (no added nitrobenzene) and Cu-Selemion, and (d) methanol (no added nitrobenzene) and Cu,Pt-Nafion.

The reaction products obtained in the electroreduction of nitrobenzene are known to vary with electrode material, potential, acidity, temperature, etc.[12,13)] In a highly acidic solution, aniline (6 electron process) and *p*-aminophenol, which is produced *via* rearrangement of a phenylhydroxylamine intermediate (4 electron process), are obtained, while phenylhydroxylamine and dimerized products, such as azoxybenzene, hydroazobenzene, *etc,* tend to be generated in a less acidic solution. Perfluorosulfonate membranes provide a higher acidity than hydrocarbon sulfonic acid membranes because of the presence of the fluorocarbon rather than hydrocarbon groups (the fluorine atom is electron withdrawing),[14)] and the acidity of Nafion in a hydrated membrane is comparable to that of a 10 wt% H_2SO_4 solution.[15)] Hence, the acidity in the vicinity of the active site of Cu-Selemion is lower than that Cu,Pt-Nafion. In addition, the ion-exchange sites of Selemion are less dissociated in a nitrobenzene/methanol/water mixture under the electrolytic conditions. It is therefore considered that the dimerized by-product was produced due to an insufficient acidity of Selemion. This by-product was generated significantly at current densities less than 32 mA cm^{-2}.

To improve the mass transport rate of nitrobenzene and the selectivity for aniline production, the surface of Selemion was modified by coating with a thin layer of Nafion. The variations of current efficiency for aniline production and cell voltage with current density obtained with Nafion-modified Cu-Selemion are shown in Fig. 1. The cell voltage was comparable to that without Nafion-coating. The current efficiencies were as high as 90% at current densities up to 70 mA cm^{-2}, which were comparable with those obtained with Cu,Pt-Nafion. The current efficiency was greater than 80% even at a high current density of 97 mA cm^{-2}. Aniline was the sole product, and no other organic by-products were detected with HPLC. These facts show that Nafion coating can improve the mass transport rate and the reaction selectivity. The environment in the vicinity of active sites of Nafion-modified Cu-Selemion is similar to that of Cu,Pt-Nafion. Hence, the acidity is high, and the mass transport rate is enhanced. In conclusion, the SPE method using the Nafion-modified Cu-Selemion is promising for use in industrial aniline synthesis.

We are grateful to Asahi Glass Co., Ltd. for donating Selemion CMV samples. This work was partially supported by a Grant-in-Aid for the Scientific Research (No. 05235107) from the Ministry of Education, Science and Culture, Japan.

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(Received August 2, 1993)