



An electrolytic system based on the anion exchange reaction between KCl and an anion exchange resin

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ABSTRACT

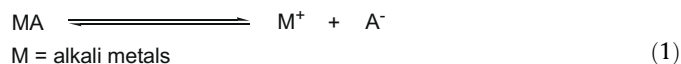
We have developed a novel electrolytic system based on the anion exchange reaction between KCl and Amberlyst A26. It was demonstrated by preparative electrolysis experiments as well as cyclic voltammetry that the anion exchange reaction offers a unique electrolytic system for electroreduction of organic compounds. On the basis of the electrolytic system, electroreduction of aromatic carbonyl compounds was successfully achieved by using an undivided cell to provide the corresponding coupling products as pinacols in good to high yields with high diastereoselectivity.

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1. Introduction

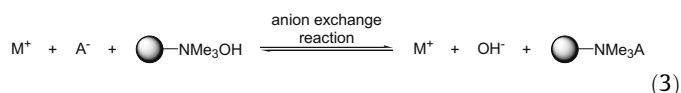
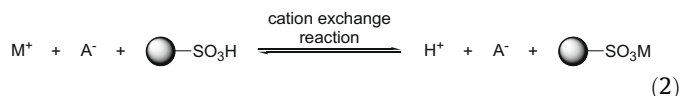
From the viewpoints of economical and environmental impacts, naturally occurring inorganic salts and their derivatives are more ideal supporting electrolytes compared to synthetic quaternary ammonium salts. However, inorganic salts generally have poor solubility in organic solvents to restrict their use in organic electrosynthesis, while quaternary ammonium salts are commonly used owing to their good solubility in organic solvents. In order to enhance the dissociation of alkali metal salts in aprotic organic solvents (Eq. (1)), we have recently developed a novel electrolytic system based on the cation exchange reaction between alkali metal salts and cation exchange resins (Eq. (2)). The cation exchange reaction promotes the dissociation of alkali metal salts in aprotic organic solvents by shifting the equilibrium to the right, and the resulting ions play the role of supporting electrolytes. On the basis of the electrolytic system, anodic oxidation [1], indirect anodic oxidation [2], and anodic fluorination [3] of organic compounds have been successfully achieved by using an undivided cell, because H^+ derived from the cation exchange reaction is exclusively reduced at the cathode. However, it was difficult to apply the electrolytic system to electroreduction of organic compounds because of the limited cathodic potential win-

dow. In order to expand the methodology to electroreduction of organic compounds, we next focused on the anion exchange reaction between alkali metal salts and anion exchange resins (terminal group: NMe_3OH) (Eq. (3)). The anion exchange reaction would promote the dissociation of alkali metal salts such as KCl in aprotic organic solvents to generate the corresponding ions as supporting electrolytes. In addition, OH^- derived from the anion exchange reaction should be predominantly oxidized at the anode. Therefore, the anion exchange reaction would offer a unique electrolytic system for electroreduction of organic compounds using an undivided cell. With these facts in mind, we herein report an electrolytic system for electroreduction of organic compounds based on the anion exchange reaction between KCl and an anion exchange resin.



M = alkali metals

A = halogens, BF_4



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2. Experimental

2.1. General

^1H NMR spectra were recorded on a JEOL JNM EX-270 (^1H : 270 MHz) spectrometer in CDCl_3 with tetramethylsilane (TMS) as an internal standard. EI mass spectra were recorded on a Shimadzu PARVUM2 gas chromatograph–mass spectrometer.

2.2. Materials

Amberlyst A26 (terminal group: NMe_3OH , loading: 4.2 mmol g^{-1}) was purchased from Aldrich and used after decantation. All other reagents were purchased from commercial suppliers and used without further purification.

2.3. Cyclic voltammetry

Cyclic voltammetry was performed by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 610B). Cyclic voltammetry was carried out with a three-electrode system using a glassy carbon disk working electrode ($\phi = 1 \text{ mm}$), a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode.

2.4. General procedure for electroreduction of aromatic carbonyl compounds based on the anion exchange reaction between KCl and Amberlyst A26

Preparative electrolysis experiments were carried out with a DC power supply (Matsusada Precision PK-80H). Electroreduction of an aromatic carbonyl compound was carried out with a platinum plate anode ($2 \times 2 \text{ cm}^2$) and a glassy carbon plate cathode ($2 \times 2 \text{ cm}^2$) in DMF (10 ml) containing KCl (1 mmol) and Amberlyst A26 (5 mmol based on the NMe_3OH group) using an undivided cell. Constant current electrolysis (10 mA cm^{-2}) was conducted with magnetic stirring at room temperature. The conversion of the substrate was monitored by TLC. After the electricity was passed until the complete consumption of the substrate, the electrolytic solution was passed through a glass filter (pore size: $5\text{--}10 \mu\text{m}$) to remove Amberlyst A26. The filtrate was added to water and extracted with diethyl ether. The combined extracts were dried over anhydrous MgSO_4 . After removal of the drying reagent, the organic layer was concentrated under reduced pressure and the residue was purified over silica gel column to obtain the product, which was identified by comparison with literature values (**2** [4], **4** [5], **6** [4], **8** [5], and **10** [6]) using ^1H NMR and mass spectroscopy.

2.5. Regeneration of the spent Amberlyst A26

After the spent Amberlyst A26 was washed with MeOH (100 ml), it was regenerated by treating with 1 M aq. KOH (100 ml). The regenerated Amberlyst A26 was washed with MeOH (20 ml) and DMF (20 ml), and then used in the recycling experiments.

2.6. Determination of the end-point of the anion exchange reaction between KCl and Amberlyst A26 in MeCN by acid–base titration

After MeCN solution (10 ml) containing KCl (1 mmol) and Amberlyst A26 (5 mmol based on the NMe_3OH group) was stirred for 2 h, the Amberlyst A26 was separated from the solution by filtration and washed with MeCN (100 ml). It was added to water (10 ml), and the solution was titrated with 0.30 M aq. HCl using phenol red as a pH indicator.

3. Results and discussion

3.1. Electrochemical investigation of the anion exchange reaction between KCl and Amberlyst A26

In order to verify the anion exchange reaction between KCl and Amberlyst A26 (strongly basic anion exchanger, terminal group: NMe_3OH), we first measured the cyclic voltammograms of KCl and Amberlyst A26 in DMF, respectively. As shown in Fig. 1a, the oxidation current for Cl^- was hardly observed in the presence of KCl. This seems to be due to the low solubility of KCl in DMF [7]. On the other hand, although Amberlyst A26 is a strong base, the oxidation current for OH^- was not observed at all as shown in Fig. 1b. In addition, ionic conductivity was hardly provided in this case. These findings mean that the ion pair of the NMe_3^+ cation and OH^- is held together by Coulomb force, which makes it difficult to provide sufficient ionic conductivity to the DMF solvent. In contrast, in the presence of both KCl and Amberlyst A26, the oxidation current for OH^- and the reduction current for K^+ were clearly observed as shown in Fig. 1c. These results indicate that the anion exchange reaction between KCl and Amberlyst A26 occurs in DMF to promote the dissociation of KCl, and the resulting ions seem to play the role of supporting electrolytes.

3.2. Optimization of the electrolytic system based on the anion exchange reaction between KCl and Amberlyst A26

It is well known that electroreduction of aromatic carbonyl compounds in alkaline solution preferentially gives the corresponding coupling products as pinacols [8]. We then chose the electroreduction of acetophenone (**1**) as a model reaction to optimize the electrolytic system based on the anion exchange reaction between KCl and Amberlyst A26 as shown in Table 1.

Electroreduction of **1** was attempted in the absence of Amberlyst A26, however, it was difficult to perform the electrolysis owing to the extremely high cell voltage (Entry 1). In contrast, in the presence of Amberlyst A26, electroreduction of **1** took place to provide the corresponding coupling product **2** in good yield (Entry 2). However, the cell voltage was relatively high (ca. 25 V). The cell voltage decreased to less than 10 V with increasing the amount of Amberlyst A26 (Entry 3). In addition, **2** was obtained in high yield with higher diastereoselectivity, which is consistent with the previous report [9]. These results indicate that the electrolytic system based on the anion exchange reaction between KCl and Amberlyst A26 is

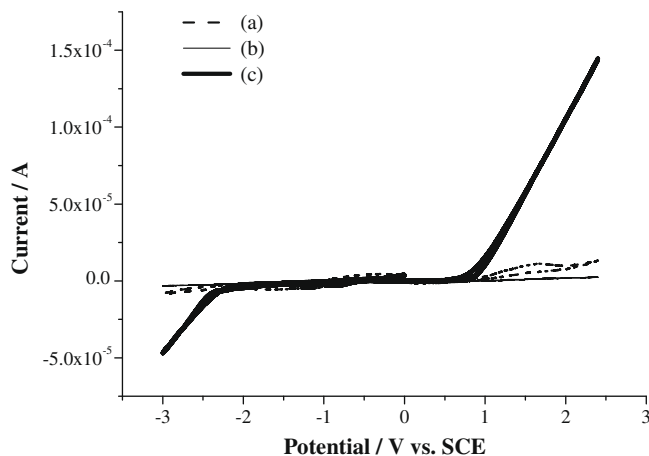


Fig. 1. Cyclic voltammograms of (a) KCl (1 mmol), (b) Amberlyst A26 (5 mmol based on the NMe_3OH group), and (c) KCl (1 mmol) and Amberlyst A26 (5 mmol) in DMF (10 ml), recorded at a glassy carbon disk electrode ($\phi = 1 \text{ mm}$). The scan rate was 100 mV s^{-1} .

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