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Preparation and Application of New Modified Electrodes Bearing the Crown Ether – Alkali Metal Ion Complexes

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We have recently attained the paired electrolysis which consists of the combination between the cathodic reduction of aliphatic esters **1** and the anodic oxidation of THF (solvent) affording 2-alkoxytetrahydrofuran **4** (**Scheme 1**).[1, 2] It has also been demonstrated that the use of supporting electrolytes containing alkali metal ions such as $LiClO_4$ is very important to promote the electroreduction of **1** and the use of tetraalkylammonium salts such as Bu_4NClO_4 is not effective. The electron transfer to **1** from cathode is probably mediated by the electrogenerated active reductant (mediatory system). The active reductant, probably the alkali metal (0), is expected to be generated in the electrical double layer and its life time in the electrolysis solution is considerably short. Therefore, in order to enhance the reaction efficiency it is promising to fix the mediatory centers on the electrode surface and to restrict the diffusion of the mediators into the electrolysis solution. In this study it has been proposed new electroreduction systems using the modified electrode having the complexes of alkali metal ion with crown ether type ligands as mediatory centers. Additionally we have further investigated the effect of magnesium ion as an electron transfer catalyst in this electroreduction system.

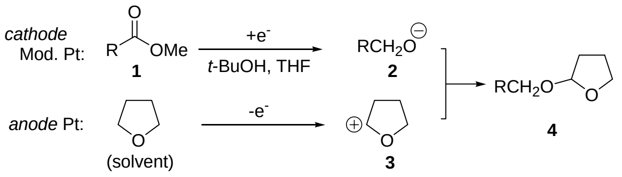
Three kinds of chemically modified platinum electrodes fixing alkali metal ions as mediatory centers were prepared by simple procedures, that is, the crown ether type ligands (*Mod.Pt(A)*, *Mod.Pt(B)*, and *Mod.Pt(C)*) were modified on the surface of platinum electrodes with siloxane bonding between the anodically oxidized platinum electrode (*Pt/PtO*) and triethoxysilyl groups in the crown ether type ligands. And alkali metal ions were then coordinated by the crown ether ligands on the platinum electrode (**Scheme 2**). The plausible structures of these modified platinum electrodes having the complexes of sodium ion with crown ether type ligands (*MPt(A)-Na*, *MPt(B)-Na*, *MPt(C)-Na*) were illustrated in **Figure**.

The compositions of chemical elements on the surface of the resulting modified platinum electrodes (*MPt(A)-Na*, *MPt(B)-Na*, *MPt(C)-Na*) were characterized by X-ray photoelectron spectra (ESCA). The present characterization could not give the absolute quantitative information of respective chemical elements, but was clearly observed Na 1s band at *ca.* 1070 eV, which indicated the complexation of sodium ion with the ligands on the surface of platinum electrode.

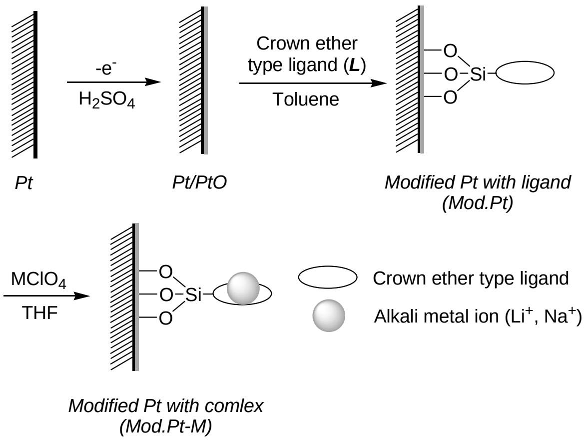
The electroreduction of methyl decanoate (**1**) was carried out using the modified platinum electrodes in the presence of *t*-BuOH as a proton donor and Bu_4NClO_4 as a supporting electrolyte to afford **4**, while the use of the untreated platinum electrode was ineffective to the electroreduction of **1** (**Table**). The use of the modified platinum electrodes having the complex of sodium ion with the polymeric ligands, *Mod.Pt(B)-Na* and *Mod.Pt(C)-Na*, gave the reduced product in 52% and 47% yields respectively. The use of $NaClO_4$ as a supporting electrolyte was found to increase the yield of the reduced product (69%). Moreover, in the presence of anodically dissolved magnesium ion using the modified platinum electrode *Mod.Pt(C)-Na* was obtained the reduced product 96% yield. The role of the anodically dissolved magnesium ion remains to be established, however, it is plausible that the reduction potential of aliphatic ester is positively shifted by the coordination of magnesium ion as a Lewis acid to the ester.

References

[1] M. Ishifune et al. *Electrochimica Acta* **2003**, *48*, 1879-1884.
[2] M. Ishifune et al. *Electrochimica Acta* **2001**, *46*, 3259-3264.



Scheme 1. Paired electrolysis system of combination between cathodic reduction of aliphatic esters and anodic oxidation of THF (solvent).



Scheme 2. Preparation of modified platinum electrode having the complex of alkali metal ion with crown ether type ligand.

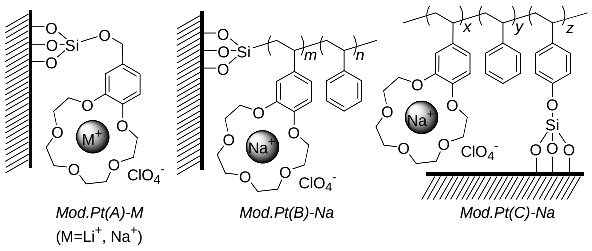


Figure. Modified platinum electrodes having the complex of alkali metal ion with crown ether type ligand.

Table Electroreduction of Methyl *n*-Decanoate using Mod Pt Cathode

cathode	supporting electrolyte	Mg ion[a]	yield of **4**, %
Pt	*n*-Bu_4NClO_4	—	trace
Mod. Pt (A)-Na	*n*-Bu_4NClO_4	—	46
Mod. Pt (B)-Na	*n*-Bu_4NClO_4	—	52
Mod. Pt (C)-Na	*n*-Bu_4NClO_4	—	47
Mod. Pt (C)-Na	$NaClO_4$	—	69
Mod. Pt (C)-Na	$NaClO_4$	0.3 equiv. based on **1**	96

The electroreduction was carried out in the solution of supporting electrolyte in THF in the presence of 6 equiv. of *t*-BuOH as a proton donor. The electricity was 7 F/mol.
[a] Mg ion was anodically dissolved. The pre-electricity was 300C.