SEPARATION AND RECOVERY OF PLATINUM GROUP METALS FROM AUTOMOTIVE CATALYSTS USING POLYMER INCLUSION MEMBRANES CONTAINING IONIC LIQUIDS

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（イオン液体を含むポリマー包接膜を使用した自動車触媒からの白金族金属の分離と回収）

論 文 内 容 の 要 旨

The demand for PGMs was steadily rising in the past several years and is predicted will be continuously growing in the future. Since the amount of primary ores is limited and the role of PGMs in the manufacture of various products is arguably irreplaceable, the need to recover PGMs from end-of-life products as a secondary source is inevitable. Furthermore, using wastes as resources is also favorable from the perspective of environmental ethics since it would decrease the necessity to excavate more mining sites and prevent harmful material disposal into landfill. As such, automotive catalyst wastes meet the criteria of secondary resources as they possess PGM-rich content and are widely available, i.e., proportional to the number of cars in the world. However, adequate and green technology for the separation and recovery of PGMs are quite challenging issues. The present thesis addresses those issues by developing PIM technology specifically designed to recover PGMs, using $P_{88812}Cl$ ionic liquid as the metal carrier.

In Chapter 2, PIMs containing the $P_{88812}Cl$ ionic liquid was developed, and the transport performance in the separation of Pd(II) and Rh(III) was systematically investigated. The optimum PIM composition was 50 wt% PVDF-*co*-HFP (base-polymer), 40 wt% $P_{88812}Cl$ (carrier), and 10 wt% 2NPOE (plasticizer). In the experiments to selectively transport Pd(II) from the feed to receiving solutions, several factors affected the transport kinetics and selectivity, including the concentration of HCl in the feed solution, the concentration of thiourea in the receiving solution, and the initial metal concentration. At the optimized condition, selective transport of Pd(II) with a recovery yield of 98% and purity of 99% could be achieved, while Rh(III) remained in the feed solution. As a comparison, PIMs containing a commercially available $P_{66614}Cl$ ionic liquid were also prepared. The PIM containing $P_{88812}Cl$ demonstrated a stable performance over a 7-cycle of reusability test, while the PIM containing $P_{66614}Cl$ exhibited approximately 30% depletion in the ability to transport Pd(II) selectively. The remarkable performance of $P_{88812}Cl$ ionic liquid to function as a carrier could be attributed to its higher hydrophobicity but lower viscosity compares to those of its commercially available counterpart. These promising results became a useful insight to carry out further investigation.

In Chapter 3, a strategy to perform separation of three PGMs, i.e., Pt(IV), Pd(II), and Rh(III), using the PIM developed in Chapter 2 was established. Sequential transports using a one-pot system with one membrane were carried out. In the first transport sequence, Pt(IV) could be

selectively transported with the recovery of 96% and purity of 89.9%, while Pd(II) and Rh(III) stayed in the feed solution. The selective Pt(IV) transport was driven by an appropriate receiving solution, which was 0.1 M $NaClO_4$ in 1 M HCl. In the second transport sequence, Pd(II) could be transported into the receiving solution with a recovery of 96% and purity of 99.9%, while Rh(III) completely remained in the feed solution. This time, the receiving solution was a mixture of 10 mM thiourea, 0.1 M KSCN, and 1 M HCl. After the desired separation performances were achieved, transport mechanisms were studied by considering the transport behaviors and spectroscopy analyses. Pt(IV) was transported through the PIM via a coupled ion-exchange mechanism, and Pd(II) was transported via simultaneous ion exchange and ligand substitution. In addition, a membrane stability test demonstrated excellent durability of the PIM as it could maintain stable performance over the course of 4 weeks, during which sequential transports of Pt(IV) and Pd(II) were continuously carried out.

In Chapter 4, the PIMs and the transport strategy developed in Chapter 2 and Chapter 3 were applied to recover PGMs from actual waste, i.e., a spent automotive catalyst. At first, metals were leached from the automotive catalyst matrix using 2 M HCl, preceded by pretreatment using HCOOH. The leachate solution, which contains 12 metals, was subjected to membrane transport operations to recover the PGMs selectively. To study the possibility to enhance transport performances further, two types of PIM were prepared, which are membranes with isotropic and dense morphology (ID-PIMs) and membranes with anisotropic and porous morphology (AP-PIMs). Selective transport of Pt(IV) from the leachate solution could be performed through both types of PIM with recoveries of more than 90%. In the selective Pd(II) transport, ID-PIM showed a remarkable product purity (almost 100%), while AP-PIM showed rapid transport kinetics. As for Rh(III), the transport hardly occurred through ID-PIM, while it was observed to happen through AP-PIM. It was also found that the Rh(III) transport could be improved at elevated temperatures. ID-PIMs and AP-PIMs, although having the same chemical compositions, demonstrated distinctive features which are governed by the morphologies. This could be a helpful insight into the future development of PIMs. More importantly, recovery of PGMs from the spent automotive catalyst using PIMs containing the ionic liquid was successfully performed, along with unraveling the chemistry phenomena that drive the transport of the metals through the membranes.