Complexation Mechanism of Olefin with Silver Ions Dissolved in a Polymer Matrix and its Effect on Facilitated Olefin Transport

Jong Hak Kim,[a, b] Byoung Ryul Min,[b] Jongok Won,*[a] and Yong Soo Kang*[a]

Abstract: Remarkable separation performance of olefin/paraffin mixtures was previously reported by facilitated olefin transport through silver-based polymer electrolyte membranes. The mechanism of facilitated olefin transport in solid membranes of $AgCF_3SO_3$ dissolved in poly(N-vinyl pyrrolidone) (PVP) is investigated. In silver polymer electrolyte membranes, only free anions are present up to the 2:1 mole ratio of [C=O]:[Ag], and ion pairs start to form at a ratio of 1:1, followed by higher-order ionic aggregates above a ratio of 1:2. At silver concentrations above 3:1, the propylene permeance increases almost linearly with the total silver concentration, unexpectedly, regardless of the silver ionic constituents. It was also found that all the silver constituents, including ion pairs and higher order ionic aggregates, were completely redissolved into free anions under the propylene environment; this suggests that propylene can be a good ligand for the silver cation. From these experimental findings, a new mechanism for the complexation reaction between propylenes and silver salts in silver–polymer electrolytes was proposed. The new mechanism is consistent with the linearity between the propylene permeance and the total silver concentration regardless of the kind of the silver constituents. Therefore, the facilitated propylene transport through silver–polymer electrolytes may be associated mainly with the silver cation weakly coordinated with both carbonyl oxygen atoms and propylene.

Keywords: facilitated transport · membranes · polymer electrolyte · polymers · propylene · silver

Introduction

Polymer electrolytes are composed of metal salts dissolved in a polymeric matrix. Thus, the dissolving behavior and ionic constituents of metal salts in the polymer matrix are very important in determining physical properties, particularly the ionic conduction and mass transport properties.[1–4] Mass transport properties through silver-based polymer electrolyte membranes have been paid much attention recently, in addition to traditional applications to secondary batteries, fuel cells, and electrochromic displays[5–9] because they exhibit facilitated olefin transport and may possibly be applied to separation of olefin/paraffin mixtures.[10–15]

It has been well known that silver ions react with olefins reversibly and specifically and, thus, act as an olefin carrier for facilitated transport.[16] In this respect, the call has been for the exploration of facilitated transport membranes as a route to stemming the tide of enormous energy consumption of conventional distillation processes. We have reported the facilitated olefin transport based on silver–polymer electrolytes made of $AgBF_4$ or $AgCF_3SO_3$ dissolved in poly(2-ethyl-2-oxazoline) (POZ) or poly(*N*-vinylpyrrolidone) (PVP).[10–13] The propylene permeance increased remarkably from 0.0312 GPU ($1\,GPU = 1.0 \times 10^{-6}\,cm^3(STP)\,cm^{-2}\,s^{-1}cm\,Hg^{-1}$) to nearly 45 upon incorporation of $AgBF_4$ in PVP or POZ up to the 1:1 mole ratio of [C=O]:[Ag] at 138 kPa propylene pressure and ambient temperature. However, the propane permeance decreased monotonically upon incorporation of the silver salt from 0.0324 to 0.003 GPU. Thus, the ideal separation factor of the propylene over propane reached almost 15000, that is, propylene permeates through the polymer electrolyte membrane 15000 times faster than propane.

Separation performance through silver-based polymer electrolyte membranes was remarkably high. However, the mechanism of facilitated olefin transport in solid-state polymer electrolytes, in particular the interaction of olefins with silver ions, is poorly understood. Therefore, the investigation on the structure of solid polymer electrolytes and their interaction with olefin is necessary in order to give insights into the facilitated transport mechanism through solid polymer electrolyte membranes.

---

[a] Dr. Y. S. Kang, Dr. J. Won, J. H. Kim
Center for Facilitated Transport Membranes
Korea Institute of Science and Technology P. O. Box 131
Cheongryang, Seoul 130-650 (South Korea)
Fax: (+82) 2-958-6869
E-mail: yskang@kist.re.kr

[b] J. H. Kim, Dr. B. R. Min
Department of Chemical Engineering, Yonsei University
Seoul 120-749 (South Korea)

0947-6539/02/0803-0650 $ 17.50+.50/0

When metal salts are dissolved in a polymer matrix, they may exist as free ions, contact ion pairs, or ionic aggregates depending on both the concentration of the metal salt and the intensity of the interaction between the metal salt and polymer matrix. Further the interaction of olefin with silver in polymer electrolytes will depend on the kind of the ionic constituents.

In this regards, the ionic constituents of $AgCF_3SO_3$ dissolved in poly(*N*-vinylpyrrolidone) (PVP) in a propylene environment will be characterized first, and the role of the various ionic constituents on facilitated propylene transport and their interaction mechanism with propylene will be investigated.

Experimental Section

Poly(*N*-vinylpyrrolidone) (PVP) ($M_w = 1 \times 10^6$) and silver trifluoromethanesulfonate (silver triflate, $AgCF_3SO_3$) were purchased from Aldrich and were used without further purification. The appropriate amounts of PVP and silver triflate depending on the mole ratio of [C=O]:[Ag] were dissolved in methanol to be 10 wt% polymer solution. The solution was then cast on a teflon–glass plate and dried under N_2 environment. The films were further dried in a vacuum oven for at least two days at room temperature. Raman spectra were collected for PVP/$AgCF_3SO_3$ electrolytes at room temperature with a Perkin–Elmer System 2000 NIR FT-Raman spectrometer. This experimental apparatus included a neodymium-doped yttrium aluminum garnet (NdYAG) laser operating at 1064 nm. IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64—200 scans were signal-averaged at a resolution 2 cm^{-1}. Raman and IR spectroscopic characterization were performed with a pressure cell equipped with quartz and CaF_2 windows, respectively. The gas permeation experiments were carried out by means of the constant pressure/variable volume method. Especially, in lower gas permeances such as propane permeances below 1:2 of [C=O]:[Ag], constant volume/time lag method was employed for the exact results. For the gas permeation test, the polymer solution was coated onto an asymmetric microporous substrate (SEAHAN Industries, Seoul, Korea) with a RK Control Coater. After evaporation of solvent in a convection oven at 40 °C under nitrogen, the membrane was dried completely in a vacuum oven for two days at room temperature. The thickness of the top polymer electrolyte layer was approximately 1 µm and the pressure difference was 413.5 kPa.

Results and Discussion

Ionic constituents: Figure 1 shows the Raman spectra in the region of the $\nu_s(SO_3^-)$ stretching mode with varying mole ratio of [C=O]:[Ag]. The ionic constituents of PVP/$AgCF_3SO_3$ were recently characterized based on the $\nu_s(SO_3^-)$ mode.[17] The $\nu_s(SO_3^-)$ stretching band was deconvoluted into the cvibrations of free ions (1032 cm^{-1}), ion pairs (1038 cm^{-1}), and higher-order ionic aggregates (1048 cm^{-1}), and the concentration of each constituent was calculated based on the fact that the relative concentration of each ionic constituent is directly proportional to its relative intensity.[6–8] Thus, it was found that only free ions are present up to a mole ratio of [C=O]:[Ag] of 2:1, while ion pairs start to form at ratios of 1:1, followed by higher-order ionic aggregates at ratios of 1:2. It is interesting to note that free ions are not observable at 1:3 mole ratio of [C=O]:[Ag].

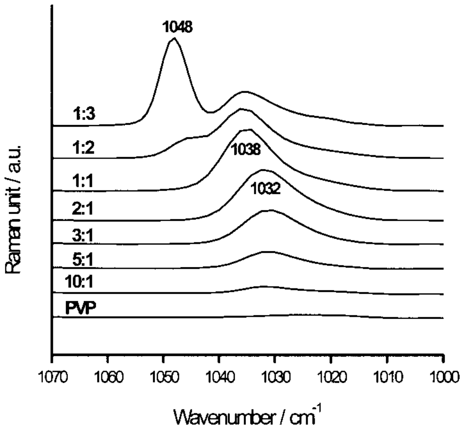


Figure 1. The $\nu_s(SO_3^-)$ modes in FT-Raman spectra of pure PVP and PVP/$AgCF_3SO_3$ complexes with various [C=O]:[Ag] mole ratios.

Gas transport properties: Figure 2 shows the pure gas permeances of propylene and propane through the PVP/$AgCF_3SO_3$ electrolyte membranes with varying silver concentration. In addition, the inset shows the corresponding selectivity of propylene over propane. The permeances of propylene and propane did not vary significantly up to 3:1 (0.25 mole fraction of silver ions) and 1:1 (0.5 mole fraction) mole ratio of [C=O]:[Ag], respectively. However, the permeance of propylene enhanced sharply at silver concentrations above 3:1, nearly in linear proportion to the silver concentration, demonstrating the facilitated propylene transport.[10] The linear increase in the permeance with the total silver concentration regardless of the presence of different ionic constituents is very characteristic, because the role of each ionic constituent for the facilitated transport is expected to be different.

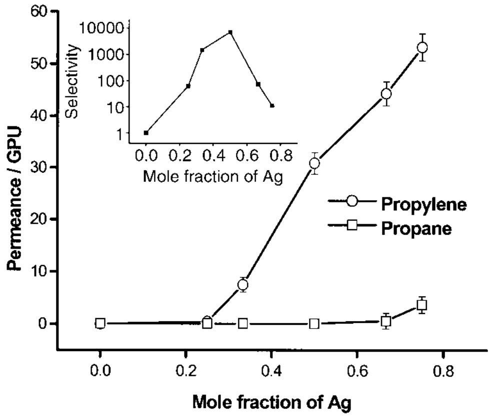


Figure 2. Permeance of propylene and propane and selectivity in PVP/$AgCF_3SO_3$ as a function of silver concentration.

In the mean time, the permeance of propane decreased from 0.0324 to 0.0044 GPU with the silver concentration below 1:1 although the decrease is not clearly shown in Figure 2. It started to increase slightly from 1:2 of [C=O]:[Ag] and further increased at 1:3. This may be due to the fact that the structural defects of PVP/$AgCF_3SO_3$ electrolytes, which is considered to be caused by the incompatibility between polymer matrix and higher order ionic aggregates, were possibly formed, and, consequently, the permeances of both propylene and propane increased simultaneously, resulting in a lower selectivity. Upon this, although the permeance of propylene might also contain the gas transport through the structural defects of membranes as well as facilitated transport, the former appeared to be so much lower and buried in the error range of the latter.

Redissolution of silver salts into free anions upon propylene sorption: Silver ion constituents may possibly change in the propylene environment. Thus, the time evolution Raman spectra of the $\nu_s(SO_3^-)$ symmetric stretching band for the 1:3 PVP/AgCF$_3$SO$_3$ at propylene pressure of 275.6 kPa were obtained and are displayed in Figure 3. Propylene itself is nonactive in the range of Raman spectra. The 1:3 PVP/AgCF$_3$SO$_3$ membrane before propylene contact is made up of nearly 0.0 % free ions, 42.7 % ion pairs, and 57.3 % ion aggregates, according to the deconvolution of the peaks. When propylene molecules are in contact with polymer electrolytes, they will coordinate with silver ions and will be dissolved. As the contact time of propylene with the polymer electrolytes was increased, the band intensities of both ion aggregates at 1048 cm^{-1} and ion pairs at 1038 cm^{-1} gradually decreased, whereas a new shoulder peak around at 1032 cm^{-1} was apparent and became prominent with time, implying the regeneration of free SO$_3^-$ ions. Interestingly, after 24 hours, the only band associated with the free SO$_3^-$ ion was observed, indicating that ion aggregates and ion pairs were not present. This notable observation clearly represents that propylene can be a good ligand for the silver ions dissolved in the polymer matrices and can coordinate with the silver ions of ion aggregates and ion pairs, resulting in redissolution into free anions. The redissolution of ion aggregates and ion pairs in PVP/AgCF$_3$SO$_3$ electrolytes under the propylene environment is possible because the coordination sites of the silver ion can be occupied by π electrons of propylenes and, consequently, weaken the interaction of the silver cation with its counter anion. The enhanced strength of the complexed C=O bond in the propylene environment is also evidenced by IR spectroscopy and will be discussed in the next section.

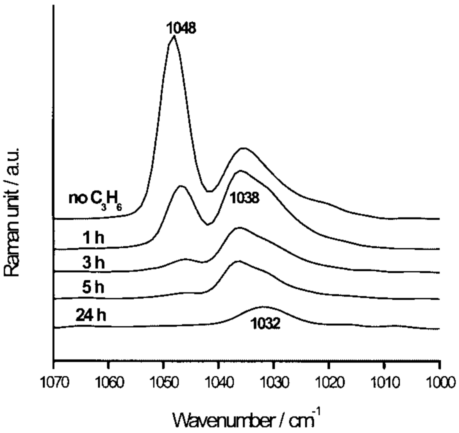


Figure 3. Time-evolution Raman spectra for $\nu_s(SO_3^-)$ mode in 1:3 PVP/AgCF$_3$SO$_3$ absorbing propylene (275.6 kPa).

Therefore, propylene acts as a solvent for silver–polymer electrolytes by accelerating the ion solvation, which is usually found in gel type polymer electrolytes.[18, 19] For other compositions, for example, 2:1, 1:1, 1:2, almost identical results were obtained (not shown here), that is, that all the silver salts are solvated into free anions.

In summary, all the ionic constituents of the silver salt including ion pairs and aggregates in PVP/AgCF$_3$SO$_3$ became free ions under the equilibrium propylene sorption and, thereby, played an important role in the facilitated olefin transport. Nevertheless, too many ion aggregates may lead to the defects of the membrane, causing a concurrent increase in the permeance of propane and resulting in a reduced selectivity of propylene over propane.

Another intriguing feature is that the band intensity before the propylene sorption was strong, but it decreased dramatically after the propylene sorption and the only small peak at 1032 cm^{-1} was observed. This may be attributed to the swelling phenomena of silver–polymer electrolytes under the propylene sorption, which is supposed to dramatically reduce the anion concentration of the direct-measuring volume with Raman scattering laser source. The swelling phenomena is supported by the results that the propylene solubility is remarkably increased from 3 cm^3(STP) cm^{-3} for pure PVP at 275.6 kPa up to 160 cm^3(STP) cm^{-3} for the 1:1 PVP/AgCF$_3$SO$_3$ electrolyte.[13]

Partial recovery of bond strength of complexed carbonyl upon propylene sorption: Figure 4 displays the FT-IR spectra of PVP and the PVP/AgCF$_3$SO$_3$ complexes with and without propylene sorption as a function of the silver salt concentration. The carbonyl stretching band shifts from 1670 cm^{-1} for pure PVP to 1634 cm^{-1} for the complexed PVP with silver ions. The band shift toward a lower wavenumber is considered to be due to the weakened strength of the carbonyl double bond induced by the coordinative interaction between the silver ion and carbonyl oxygen atom. From 1:1 to 1:3 compositions, the position and shape of the C=O band in PVP/AgCF$_3$SO$_3$ complexes before the propylene sorption

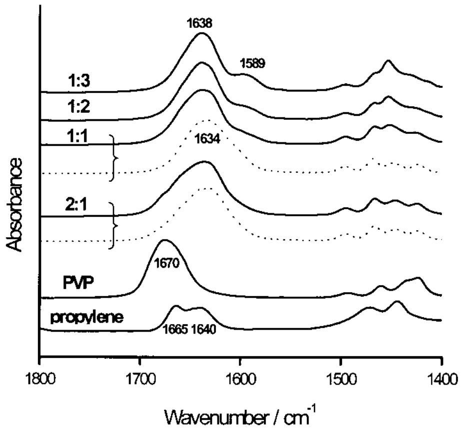


Figure 4. FT-IR spectra of PVP/AgCF$_3$SO$_3$ electrolytes with and without propylene sorption for a various mole ratios of [C=O]:[Ag]. The solid and the dotted lines represent the data with and without propylene, respectively. For pure PVP, the spectrum of PVP with propylene nearly coincide with that without propylene sorption.

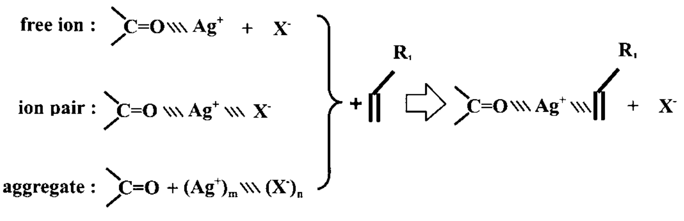
remained almost invariant, and only one spectrum (dotted line) was displayed for simplicity.

When the PVP/$AgCF_3SO_3$ electrolytes were exposed to 275.6 kPa of propylene for one hour and successively purged with nitrogen for less than one second, a new shoulder peak at 1589 cm^{-1} appeared and evolved with the silver salt concentration. The new peak at 1589 cm^{-1} is assigned to the C=C stretching vibration of propylene coordinated to the silver ion.

The position of the main peak, associated with the complexed C=O group with silver ion, moved to a higher wavenumber from 1634 to 1638 cm^{-1} after the propylene sorption. The shift of the C=O band may be comprehended by the fact that silver ions coordinated with carbonyl oxygen atoms interact with the π electrons of propylene molecules, and, hence, the carbonyl bond strength is only partially recovered relative to that before the propylene sorption. This incomplete recovery to 1670 cm^{-1} of the uncomplexed free carbonyl implies that the carbonyl oxygen atom maintains its coordinative bond with the silver ion, although the C=O bond is strengthened, and that the complete change of the complexed C=O into the free C=O upon propylene sorption is not favorable.

The spectra in the range of 1750–1550 cm^{-1} were deconvoluted into the individual peaks, that is, free C=O of PVP (1670 cm^{-1}), complexed C=O of PVP (1638 cm^{-1}), and coordinated C=C of propylene (1589 cm^{-1}), as provided in Figure 5. It is apparent that the fractional area of the coordinated C=C vibration peak increases in proportion to the silver salt concentration. Thus, it can be anticipated that more propylene molecules are soluble in PVP/$AgCF_3SO_3$ electrolytes when more silver salts are loaded.

Complexation mechanism of propylene with silver salts: From the results of FTIR and Raman spectra in PVP/$AgCF_3SO_3$ electrolytes upon absorbing propylene, it was found that 1) ion pairs and ion aggregates in the silver–polymer electrolytes are converted into free anions (spectroscopically observed) under the propylene environment and 2) the coordinative bond between the silver ion and carbonyl oxygen atom is maintained, but becomes weakened upon propylene sorption. Therefore, a possible mechanism of the complexation between propylene and silver polymer electrolytes is proposed as follows:



Therefore, the linear relationship between the propylene permeance and the total silver concentration regardless of the kind of the silver constituents could be explained by the new complexation mechanism proposed in this research.

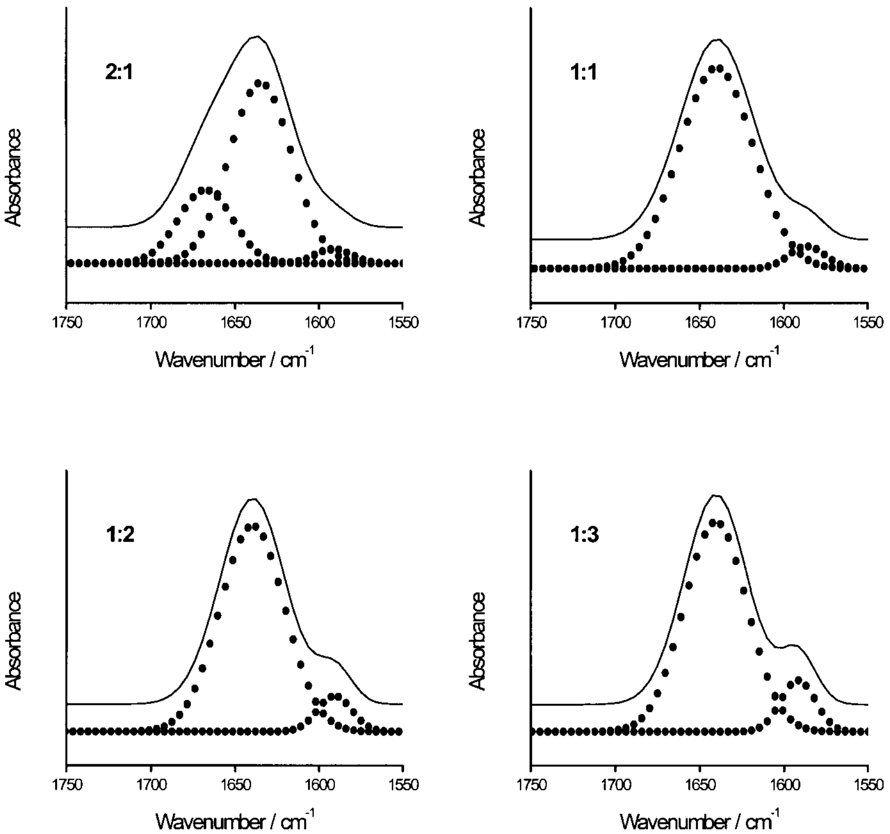


Figure 5. The deconvoluted curves of PVP/$AgCF_3SO_3$ electrolytes absorbing propylene in the range of 1750–1550 cm^{-1} from Figure 4. The assignment is as follows: free C=O of PVP (1670 cm^{-1}), complexed C=O of PVP (1638 cm^{-1}), and complexed C=C of propylene (1589 cm^{-1}).

Conclusion

It was found that free ions, ion pairs, and ion aggregates were present in silver–polymer electrolytes. The free-ion concentration decreased unexpectedly as the silver concentration increased and approached to nearly zero for the 1:3 PVP/$AgCF_3SO_3$ electrolyte.

In a propylene environment, propylene becomes a ligand for silver cation and occupies the partial coordination sites of the silver cation to make a silver complex that contains both carbonyl oxygen atom and propylene. The initial strong bond between the silver cation and carbonyl oxygen atom becomes weakened upon propylene sorption owing to the compensation for electrons from carbonyl oxygen atom with those from propylene. Thus, ion pairs and ion aggregates were redissolved into free ions.

On these experimental findings, a new mechanism for the complexation reaction between propylene and silver salts in silver–polymer electrolytes was proposed. The new mechanism is consistent with the linearity between the propylene permeance and the total silver concentration regardless of the kind of the silver constituents. Therefore, the facilitated propylene transport through silver–polymer electrolytes may be mainly associated with the silver cation weakly coordinated to both carbonyl oxygen atoms and propylene.

Acknowledgement

The authors gratefully acknowledged financial support from the Ministry of Science and Technology of Korea through the Creative Research Initiatives Program.

---

[1] A. Ferry, G. Orädd, P. Jacobsson, *J. Chem. Phys.* **1998**, *108*, 7426.
[2] W. Huang, R. Frech, R. A. Wheeler, *J. Phys. Chem*. **1994**, *98*, 100.
[3] S. Schantz, L. M. Torell, J. R. Stevens, *Appl. Phys.* **1988**, *64*, 2038.
[4] B. L. Papke, M. A. Ratner, D. F. Shriver, *Electrochem. Soc.* **1982**, *129*, 1434.
[5] A. Ferry, P. Jacobsson, L. M. Torell, *Electrochim Acta* **1995**, *40*, 2369.
[6] S. Chintapalli, R. Frech, *Electrochim Acta* **1998**, *43*, 1395.
[7] M. Kakihana, S. Sohantz, L. M. Torell, *J. Chem. Phys.* **1990**, *92*, 6271.
[8] G. Peterson, L. M. Torell, S. Panero, B. Scrosati, C. J. da Silva, M. Smith, *Solid State Ionics* **1993**, *60*, 55.
[9] H. Ericson, B. Mattsson, L. M. Torell, R. Rinne, F. Sundholm, *Electrochim. Acta* **1998**, *43*, 1401.
[10] Y. Yoon, J. Won, Y. S. Kang, *Macromolecules* **2000**, *33*, 3185.
[11] S. U. Hong, J. H. Jin, J. Won, Y. S. Kang, *Adv. Mater.* **2000**, *12*, 968.
[12] J. H. Kim, B. R. Min, C. K. Kim, J. Won, Y. S. Kang, *Macromolecules* **2001**, *34*, 6052.
[13] S. U. Hong, C. K. Kim, Y. S. Kang, *Macromolecules* **2000**, *33*, 7918.
[14] J. H. Ryu, H. Lee, Y. J. Kim, Y. S. Kang, H. S. Kim. *Chem. Eur. J.* **2001**, *7*, 1525.
[15] I. Pinnau, L. G. Toy, C. Casillas, US Patent 5670051, **1997**.
[16] R. B. Eldridge, *Ind. Eng. Chem. Res.* **1993**, *32*, 2208.
[17] J. H. Jin, S. U. Hong, J. Won, Y. S. Kang, *Macromolecules* **2000**, *33*, 4932.
[18] G. Feuillade, Ph. Perche, *J. Appl. Electrochem*. **1975**, *5*, 63.
[19] E. Tsuchida, H. Ohno, K. Tsunemi, *Electrochim. Acta* **1983**, *28*, 591.

Received: May 22, 2001 [F3279]