Comparison of Hydrogen Permeation Properties of Zn-Ni, Zn-Ni-Cd and Cd Coatings

Hansung Kim and Branko N. Popov
Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208

Introduction

Recently we developed an alkaline electrodeposition process to deposit good quality Zn-Ni-Cd deposits with high Ni and Zn contents.[19] The resultant Zn-Ni-Cd deposits have excellent corrosion and barrier properties. In this work, we compare the corrosion and hydrogen permeation inhibition properties of Zn-Ni-Cd deposits obtained using the alkaline process with Zn-Ni and Cd deposits obtained using commercial electrolytic baths. The permeation and kinetic parameters for hydrogen permeation such as the absorption-adsorption constant, the recombination reaction constant, the modified exchange current density and hydrogen surface coverage were determined using the Iyer *et al.*[20] model or its modified model. The mechanism of preventing hydrogen permeation for each coating will be compared and explained using the kinetic parameters obtained by fitting data to the models.

Experimental

Zn-Ni-Cd, Zn-Ni and Cd thin films were electrodeposited on low-carbon steel foils with thickness of 0.1mm and area of 3cm^2. Zn-Ni-Cd was electrodeposited from the alkaline sulfate bath developed by us at USC.[19] Zn-Ni and Cd depositions were carried out using a commercial bath obtained from SIFCO®. The other side of the steel membrane was electrodeposited with the thin layer (0.15~0.2 μm) of palladium to avoid corrosion reactions on steel. The rate of hydrogen permeation through the membranes was measured continuously as a function of time using the Devanathan-Stachurski permeation cell.[22] This cell-setup consists of two working compartments, cathodic and anodic chamber, and the membrane is placed between two chambers. The anodic compartment was filled with 0.2M of NaOH solution and potential was kept at –0.3V vs. Hg/HgO reference electrode until the background current was reduced to below 1μA/cm^2. Then, the cathodic compartment was filled with a supporting electrolyte containing 0.5M Na_2SO_4 and 0.5M H_3BO_3 buffer solution with pH=7. Nitrogen was purged on both sides through out the experiment in order to remove dissolved oxygen from the electrolytes. The membrane on the cathodic side of the cell was polarized potentiostatically, creating conditions for hydrogen evolution. Hydrogen generated on the cathodic side permeates through the membrane and gets oxidized on the anodic surface of the membrane. The steady state currents associated with anodic (permeation current) and cathodic (charging current) reactions were monitored continuously with changing the overpotential of hydrogen evolution reaction at the cathode side.

Results and Discussion

Fig. 1 shows the hydrogen permeation current of the Cd deposited steel membrane as a function of the applied cathodic potential. The cathodic side of the membrane was polarized in the negative direction to provide conditions for hydrogen evolution. Hydrogen that comes out of the anodic side is oxidized potentiostatically in order to obtain the permeation current. After stepping the potential a few times, the applied potential was switched off, and the decay curve was recorded. Using the same process, the permeation current and hydrogen evolution current of the Zn-Ni and Zn-Ni-Cd coated membranes were measured for each values of the applied overpotential.

In order to gain better understanding about the permeation inhibition properties of different coatings, it is important to evaluate the various kinetics parameters governing hydrogen permeation. As can be seen in the table 1, Zn-Ni coated steel shows the highest recombination constant (k_3). High recombination constant is beneficial in preventing the hydrogen permeation. However, it has a high value of modified exchange current density, $i_0^{'}$, explaining the preference of hydrogen evolution reaction when compared to those of Zn-Ni-Cd and Cd coated steel. The adsorption-absorption coefficient, $k^{''}$, was the largest for Cd coated steel followed by Zn-Ni and Zn-Ni-Cd. Therefore, the positive effect of the decrease in the hydrogen evolution reaction of Cd is diminished by the increased adsorption-absorption rate constant and the decreased recombination rate constant. With addition of Cd into the Zn-Ni, the Zn content in the alloy is suppressed and the corrosion potential shifts to positive values (-0.62V vs. SCE).[19] This causes the observed decrease in the exchange current density resulting in a slower discharge kinetics of hydrogen evolution. Also, there is a large increase in the value of recombination rate constant, k_3, for Zn-Ni-Cd alloy when compared to Cd and plain steel. Thus, Zn-Ni-Cd possesses excellent sacrificial protection properties and also inhibits the hydrogen permeation through the substrate.

References

1. H. Kim, B. N. Popov, K. S.Chen, J. Elecrochem. Soc. *In printing*.
2. R.N. Iyer, H. W. Pickering, M. Zamanzadeh, J. Electrochem. Soc. 136 (1990) 2463.
3. M. A. V Devanathan, Z. Stachurski, J. Electrochem. Soc. 110 (1963) 886.

Table 1 The kinetic parameters characterizing the hydrogen evolution and permeation through various coatings

Deposit (wt%)	$i_0^{'}$ (A cm^{-2})	$k^{''}$ (mol cm^{-3})	k_3 (mol cm^{-2} s^{-1})
Zn-Ni-Cd (50/28/22)	9.17×10^{-7}	1.11×10^{-6}	0.38×10^{-6}
Zn-Ni (86/14)	6.30×10^{-5}	2.10×10^{-5}	5.73×10^{-6}
Cd	6.22×10^{-9}	7.32×10^{-5}	1.66×10^{-9}

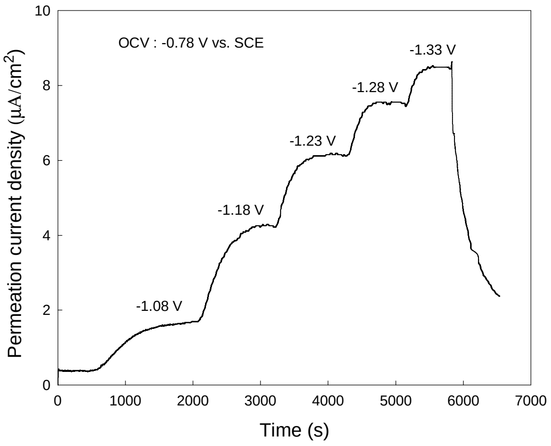

Fig. 1 The hydrogen permeation transients through Cd deposited iron membrane as a function of time for different applied cathodic potentials