Reducing Mass Transport Limitations by the Application of Special Pulsed Current Modes

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The application of periodic current or potential pulses in electrochemical systems has attracted much attention [1-4], principally with the objective of controlling the concentration of the electroactive species at the electrode/electrolyte interphase.

Cheh [1] applied the solution of Rosebrugh and Miller [2] for a current step in a finite diffusion layer to pulsed current plating concluding that the over-all pulse plating rate is always lower than that of DC plating. In *potential pulsing*, Dordi and Landau [3, 4] and Despic and Popov [5] have shown that the thickness of the equivalent boundary layer can be controlled, thereby limiting the concentration overpotential. Further, Dordi and Landau [4] have also shown that in constant amplitude *current* pulses, the boundary layer keeps growing with time.

Duhamel's theorem and the superposition principle are used here to simulate concentration profiles during periodic current application. We show that in current pulsing with constant current amplitudes and time intervals (Fig. 1), the reactant concentration profile, including its interfacial concentration is identical to that of DC application (Fig. 2), when the comparison is based on passing the same amount of charge in identical time, thus offering no advantage.

However, current pulsing with constant pulse widths but with *decreasing current density amplitudes* (Fig. 3) or current pulsing with constant current density amplitude but with *increasing relaxation times* (Fig. 4) reduces the reactant depletion or excess at the electrode. The corresponding concentration overpotentials (Fig. 5) are also lower. The advantage of current pulsing with proper selection of pulse parameters to enhance mass transfer in plating and battery applications is discussed.

References:

1. H. Y. Cheh, *J. Electrochem. Soc.*, **118**, 551 (1971).
2. T. R. Rosebrugh and W. L. Miller, *Journal of Physical Chemistry*, **14**, 816 (1911).
3. U. Landau and Y. N. Dordi, *Extended Abstracts* 79-2, 156th Meeting of The Electrochemical society, Los Angeles, CA, Oct. 14-19, (1979).
4. Y. N. Dordi, *Master's thesis,* Chemical Engineering Dept., Case Western Reserve University, Cleveland, Ohio., (1979). (U. Landau, Thesis advisor).
5. A. R. Despic and K. I. Popov, *Journal of Applied Electrochemistry*, **1**, 275 (1971).

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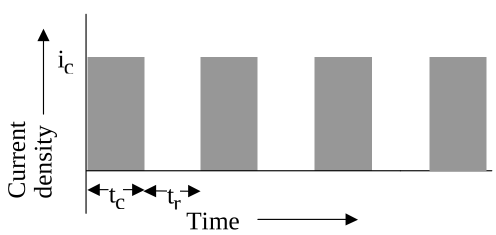

Fig. 1: Constant amplitude pulsed current interspersed with identical rest periods.

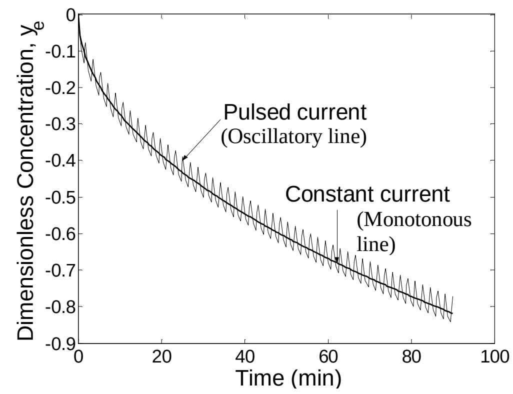

Fig. 2: Dimensionless electrode concentration, $y_e = (C_e - C_b)/C_b$*, where* C_e *and* C_b *are electrode and bulk conc., for constant amplitude current pulses with uniform relaxation periods and constant current. The average current density in both cases is 6 mA/cm*^{2}.

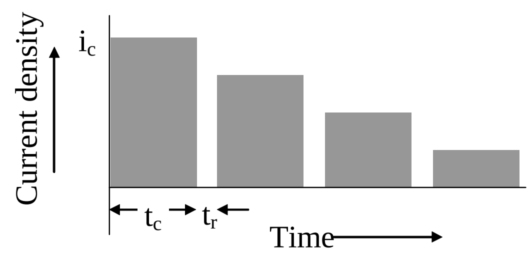

Fig. 3: A current waveform with decreasing amplitude pulses interspersed with rest periods. The cathodic pulse widths (t_c*) and the rest pulse widths (*t_r*) are constant.*

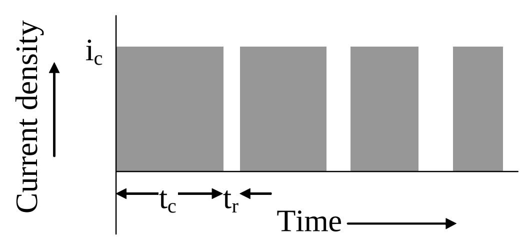

Fig. 4: A current waveform consisting of increasing magnitude current pulses interspersed with rest periods. The cathodic pulse widths decrease and the rest periods increase with time.

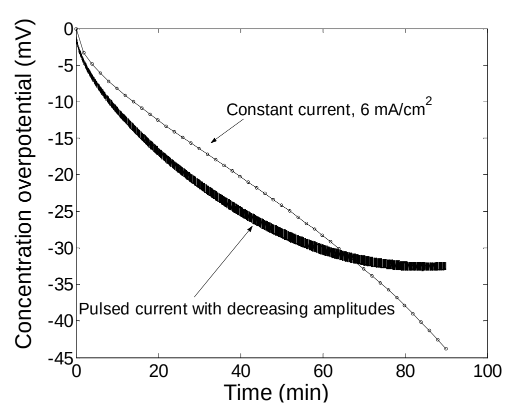

Fig. 5: The concentration overpotential for a pulse sequence shown in Fig. 3 in comparison to DC current, when both carry the same amount of charge. The concentration overpotential corresponding to the pulsed current levels off after about 66 min while the magnitude of the concentration overpotential corresponding to the DC current keeps increasing.