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FIELD	GROUP	SUB-GROUP	Surface enhanced Raman scattering; DABCO on silver; pyridine on gold; battery electrolytes; lithium surface studies.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Laser Raman spectroscopy has been coupled with electrochemical techniques such as chronocoulometry and cyclic voltammetry to study the species adsorbed on electrode surfaces and to monitor processes which occur with changes in electrode potential, solvent properties, laser exciting line wavelength, solute and other variables. Lithium metal surfaces, freshly cut in situ, in contact with THF or 2Me-THF containing LiAsF₆ or LiBF₄, have been studied with the Raman microprobe; decomposition products, polymerization and conditions for this, and photo-currents were the subject of investigation. Work has been extended to the solvents methylacetate and propylene carbonate. Studies of selected aqueous electrolyte systems have been conducted for comparison. Chronocoulometry has been used to measure pyridine adsorption at (100), (110), (111), and (311) single crystal and polycrystalline gold surfaces. In situ Raman spectra of smooth gold surfaces provided information about coverage in agreement with the isotherms from electrochemistry; the effect of surface roughness on the Raman intensity - potential profiles was measured. Photoinduced crystallization of DABCO polyiodide has been observed upon a silver electrode. The measurement of the concentration-distance profile extending from the electrode surface has been achieved with a Raman microscope. Studies of the identity and morphology of surface films that inhibit (or vice versa) the cycling efficiency of proposed lithium batteries have been studied; voltage-time transients from freshly cleaved lithium surfaces have been measured for a range of solvent-solute combinations.					
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**Vibrational Spectroscopic Studies of Electrode Surfaces and
Technologically Important Electrolyte Solutions**

by

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End of Grant Report 1987-1990

(a) Papers Published in Refereed Journals

(a.1) Fundamental Studies of the Mechanism of Surface Enhanced Raman Scattering (partially supported)

1. Surface-Enhanced Raman Scattering from Triethylenediamine (DABCO): An Electrochemical and Mechanistic Study. David A. Guzonas, Ph.D. Thesis, University of Waterloo, 1987.
2. The Surface-Enhanced Raman Scattering of the Protonated Forms of DABCO at a Silver Electrode. D.A. Guzonas, D.E. Irish and G.F. Atkinson, *Langmuir*, **5**, 787-796 (1989). (Technical Report No. 2)
3. A Raman and Infrared Spectroscopic Study of Triethylenediamine (DABCO) and Its Protonated Forms. D.A. Guzonas and D.E. Irish, *Can J. Chem.*, **66**, 1249-1257 (1988).
4. Evidence for a Photon-Driven Charge-Transfer Enhancement in the Surface Enhanced Raman Scattering of DABCO at a Silver Electrode. D.A. Guzonas, D.E. Irish and G.F. Atkinson, *Langmuir*, **6**, 1102-1112 (1990). (Technical Report No. 10)
5. A Raman Spectroscopic and Electrochemical Study of the Photoinduced Crystallization of Triethylenediamine Triiodide Upon a Silver Electrode. T. Ozeki and D.E. Irish, *J. Phys. Chem.*, in press. (Technical Report No. 8 and 18)
6. The Application of Concentration-Distance Profiling Raman Microspectroscopy to the Study of the Photoinduced Crystallization of Triethylenediamine Triiodide Upon a Silver Electrode. T. Ozeki and D.E. Irish, *J. Phys. Chem.*, in press. (Technical Report No. 19)

(a.2) Fundamental Electrochemical and Spectroscopic Studies of Pyridine Adsorption on Gold Electrode Surfaces

7. Electrochemical and Spectroscopic Study of Pyridine Adsorption on Gold Electrode Surfaces. Lorne Stolberg, Ph.D. Thesis, University of Guelph, 1990.
8. Adsorption of Pyridine at the Polycrystalline Gold Solution Interface. L. Stolberg, J. Richer, J. Lipkowski and D.E. Irish, *J. Electroanal. Chem.*, **207**, 213-234 (1986).
9. Adsorption of Pyridine at the Au(100) - Solution Interface. L. Stolberg, J. Lipkowski and D.E. Irish, *J. Electroanal. Chem.*, **238**, 333-353 (1987). (Technical Report No. 1)
10. Adsorption of Pyridine at the Au(110) - Solution Interface. L. Stolberg, J. Lipkowski and D.E. Irish, *J. Electroanal. Chem.*, **296**, 171-189 (1990). (Technical Report No. 15)
11. Adsorption of Pyridine at the Au(111) - Solution Interface. L. Stolberg, S. Morin, J. Lipkowski and D.E. Irish, *J. Electroanal. Chem.*, in press. (Technical Report No. 17)

12. Adsorption of Pyridine at the Au(311) - Solution Interface. L. Stolberg, J. Lipkowski, and D.E. Irish, J. Electroanal. Chem., in press. (Technical Report No. 20)
13. An Examination of the Relationship Between Surface Enhanced Raman Scattering (SERS) Intensities and Surface Concentration for Pyridine Adsorbed at the Polycrystalline Gold/Aqueous Solution Interface. L. Stolberg, J. Lipkowski and D.E. Irish, J. Electroanal. Chem., 300, 563-584 (1991). (Technical Report No. 16)

(a.3) **Studies of Electrolyte Solutions Relevant to Battery Studies**

14. A Raman Spectral Study of the Equilibria of Zinc Bromide Complexes in DMSO Solutions. J. van Heumen, T. Ozeki, and D.E. Irish, Can. J. Chem., 67, 2030-2036 (1989). (Technical Report No. 4)
15. A Raman Spectral Study of Solvation and Ion Association in the Systems $\text{LiAsF}_6/\text{CH}_3\text{CO}_2\text{CH}_3$ and $\text{LiAsF}_6/\text{HCO}_2\text{CH}_3$. Z. Deng and D.E. Irish, Can. J. Chem., submitted. (Technical Report No. 21)

16. Books (and Sections Thereof) Submitted for Publication (c)

"Raman Spectroscopy of Inorganic Species in Solution", Donald E. Irish and Toru Ozeki, a chapter in Analytical Raman Spectroscopy, J.G. Grasselli-Brown and B.J. Bulkin, Eds., Wiley, New York, in press. (Technical Report No. 9)

(a.4) **A New Method for the Measurement of the Concentration-Distance Profile Within the Diffusion Layer**

17. Estimation of the Concentration-Distance Profile Within the Electrochemical Diffusion Layer by Raman Microprobe Spectroscopy. T. Ozeki and D.E. Irish, J. Electroanal. Chem., 280, 451-455 (1990). (Technical Report No. 12)

Also see No. 6 above.

(a.5) **Studies of the Lithium-Electrolyte Interface**

18. Raman Microprobe In-situ and Ex-situ Study of Film Formation on Lithium/Organic Electrolyte Interfaces. M. Odziemkowski and D.E. Irish, in preparation. (Technical Report No. 6)

Also the Ph.D. Thesis of M. Odziemkowski will be completed in the first half of 1992.

(e) Technical Reports

- Total of 22

(f,g) Patents

- None

(h) Invited Presentations

- None

(i) Contributed Presentations at Scientific Society Conferences

- 23 in all; see Year End Reports 1988, 1989, 1990 and Technical Reports 3, 5, 6, 7, 8, 11, 13, 14, 22.

(j) Honours/Awards/Prizes

D.E. Irish, Marchon Lecturer, University of Newcastle upon Tyne, England, March 7-10, 1989.

Lecture Titles -

- Symmetry, Spectroscopy and Surface Studies
- Exploring the Electrode/Electrolyte Interphase with Raman Spectroscopy
- Probing the Chemistry of Aqueous Solutions at Elevated Temperatures and Pressures with Raman Spectroscopy.

D.E. Irish, Union Carbide Award for Chemical Education, Chemical Institute of Canada, 1990.

(k) Number of Graduate Students Receiving Full or Partial Support on ONR Grant

Four

- David Guzonas, Ph.D. - 1987
- Lorne Stolberg, Ph.D. - 1990
- Marek Odziemkowski, Ph.D. - in progress
- Zhongyi Deng, Ph.D. - in progress

(l) Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Grant

- Dr. Manfred Krell, University of Regensburg, Germany
- Dr. Toru Ozeki, Osaka University, Japan